Environment Canada Environnement Canada

1020926I DEST PVM EXCH COPY 03
TD 171.5.C3 R46
VOL ISS 53

REPORT EE

DEVELOPMENT OF A VEHICLE-PORTABLE ANALYTICAL SYSTEM FOR ENVIRONMENTAL EMERGENCIES

EE-53

DEVELOPMENT OF A VEHICLE-PORTABLE ANALYTICAL SYSTEM FOR ENVIRONMENTAL EMERGENCIES

by

J. Lockwood
R. Halman
M. Farrington
Farrington Lockwood Co. Ltd.
Ottawa, Ontario

This report has not undergone detailed technical review by the Environmental Protection Service and the content does not necessarily reflect the views and policies of Environment Canada. Mention of trade names or commercial products does not constitute endorsement for use.

This unedited version is undergoing a limited distribution to transfer the information to people working in related studies. This distribution is not intended to signify publication and, if the report is referenced, the author should cite it as an unpublished report of the Branch indicated below.

Any comments concerning its content should be directed to:

Environmental Emergencies Technology Division
Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 1C8

EE-53

April, 1984

FARRINGTON LOCKWOOD COMPANY LIMITED

CHEMICAL RESEARCH SPECIAL ANALYSIS

PHONE (613) 226-7314, P.O. BOX 6797, STATION "J", OTTAWA, ONTARIO, CANADA K2A 3Z4

FINAL REPORT

A REPORT ON THE FURTHER DEVELOPMENT OF THE EPS TECHNICAL SERVICES BRANCH ANALYTICAL SYSTEM

CONTRACT SERIAL NUMBER : OSS83-00065
DSS FILE NUMBER : 47SS.KE145-3-0282

SUBMITTED TO : Mr. Michel Cloutier
Project Chemist
Environmental Emergencies
Technology Division
Department of the Environment
River Road Environment
Technology Centre
River Road
Ottawa, Ontario
K1A 1C8

PREPARED BY : JUDITH LOCKWOOD
RONALD HALMAN
MIKE FARRINGTON

WORK PERFORMED : JUNE 1, 1983 TO MARCH 31, 1984

REPORT SUBMITTED : APRIL 5, 1984

ABSTRACT

This document summarizes work done, under contract KE145-3-0282, on the Level 3 analytical concept. Preliminary work on the Infrared (IR) - Ultraviolet (UV)/Visible (VIS) - TRS-80 computer system has been evaluated to determine its suitability for field use. The results are outlined.

This report also includes a summary of preliminary development work on the EETD gas chromatographic (GC) system, operating instructions and concepts behind GC analysis techniques.

The report is intended to provide sufficient information to allow appropriate decisions in the direction of future development work on the Level 3 concept. Field manuals have not been provided at this time since the preparation of this type of documentation would be premature at this stage of development work.

FOREWORD

In 1980, Environment Canada initiated a program to develop chemical spills response capability. This program, known as the Chemical Hazard Emergency Countermeasures (CHEC) Program, addresses many aspects of chemical spills including the acquisition of analytical information in the field. The analytical component of the CHEC program is divided into 5 levels of capability which are based on the accuracy and portability of the technique. The focus of this report is the Level 3 capability or "Vehicle-portable Systems".

Preliminary work on the Level 3 concept, done under contract by Concordia University, included the selection and development of computer-controlled instrumentation which would be compatible with the Level 3 concept.

In August 1983, Farrington, Lockwood Company Limited was contracted to review and assess the previous work done on the IR - UV/VIS computer concept and to initiate development work on EETD's computer-controlled gas chromatographic system.

This report summarizes the work done on both portions of the contract.

TABLE OF CONTENTS

		PAGE
ABSTRACT		i
FOREWORD		ii
TABLE OF CONTENTS		iii
LIST OF FIGURES		iv
CONCLUSIONS		v
RECOMMENDATIONS		vi
1.0	THE INFRARED (IR) - ULTRAVIOLET (UV) / VISIBLE (VIS) SPECTROPHOTOMETERS - TRS-80 COMPUTER SYSTEM	1
2.0	THE SIGMA 2000 GAS CHROMATOGRAPH (GC) - 3600 DATA STATION	4
2.1	INJECTORS	5
	2.1.1 Heated Flash Vaporization	5
	2.1.2 Split/Splitless	7
	2.1.3 Gas Sampling	9
	2.1.4 Head Space Analysis	9
2.2	DETECTORS	11
	2.2.1 Flame Ionization (FID)	11
	2.2.2 Photoionization (PID)	12
	2.2.3 Electron Capture (ECD)	14
	2.2.4 Hot Wire (HWD)	14
2.3	GAS CHROMATOGRAPHIC COLUMNS	16
2.4	3600 DATA STATION	18
2.5	LABORATORY - COMPILED DATABASE	19
	2.5.1 Software	19
	2.5.2 Database Development	20
2.6	OPERATION OF GAS CHROMATOGRAPH (GC) AND DATA STATION	21
	2.6.1 Generation of a GC Method	22
	2.6.2 Generation of a Data Handling Method	25
	2.6.3 Instrumentation Set-up	27
	2.6.4 Using Database	32
	2.6.5 Instrumentation Shutdown	33
2.7	SUITABILITY FOR FIELD USE	34
3.0	INSTRUMENTATION COMPLIANCE WITH LEVEL 3 CONCEPT	38
APPENDICES		
A	EVALUATION OF TRS-80 BASED SPECTROSCOPY SYSTEM	40
B	PRIORITY HAZARDOUS SUBSTANCES LIST	52
C	CHROMATOGRAPHY LIBRARY SYSTEM DOCUMENTATION	55
D	CALIBRATION DATA AND PLOTS	70
E	TECHNICAL SPECIFICATIONS	89

RECOMMENDATIONS

1. The TRS-80 computer should be replaced with a more appropriate data handling system. Several options are available:

- use of the P-E 3600 data station with pre-packaged operating and data manipulation software. While this is the least expensive option, it is also the least adaptable to this specific application.

- purchase of the P-E 36000 data station with pre-packaged software. This route is more expensive but would likely offer greater versatility.

- use of one of the above data systems or available micro-computers with independently-written application specific software. This option is the most expensive but could prove most useful for this specific application.

2. The level concept should be reviewed and possibly modified, based on the experience gained during the preliminary stages of this development work. Some options which are available are:

- the use of this instrumentation as part of the level 4 analytical capability, (mobile laboratory with trained personnel), with level 3 using instruments designed for field use such as MTI's Michromonitor Universal Gas Analyzer, or equivalent.

- extend the level 2 capability, with a dedicated fixed laboratory to provide additional analytical support. This option would require development of reliable sampling and rapid transportation techniques.

3. Further modification and testing of the database software should be undertaken to incorporate error trapping routines and elimination of any other problems which are encountered. Even if it is decided that the instrumentation will be used in a laboratory environment by trained personnel, this type of compound identification and quantitation software could prove very useful.

CONCLUSIONS

1. Evaluation of the IR-UV/VIS - TRS 80 instrumentation found that the data handling capabilities provided by the TRS-80 computer were inadequate to allow identification and / or quantitation of an unknown substance. Furthermore, adapting laboratory hardware to field conditions, while not impossible, would be very difficult and costly.

2. Highly trained, dedicated personnel will be required for operation of all of these instruments under field conditions, as problems must be quickly recognized and corrected in the field if reliable results are to be obtained within useful time frames.

3. As with the IR-UV/VIS instrumentation, the gas chromatographic (GC) hardware is designed for laboratory use and, as such, will be difficult to adapt to on-site spill response. While some problems are foreseen with the GC itself, major concern lies with the suitability of the Data Station for this application, as it is significantly more sensitive to its environment.

4. Major problems are anticipated with the use of unsupervised non-technical personnel as instrument operators. Specifically, the pre-packaged chromatography software provided is not sufficiently user-friendly and is not adequately supported by documentation for reliable operation by personnel without extensive training in the area.

5. Database software while operating satisfactorily, requires addition of error trapping routines to handle situations which the 3600 data station can not accommodate. Also, extensive testing of the software with real data will be required before it can be used with a high degree of confidence, in spill response situations.

sub-contracted to Underdown Chemometrics and the results of this study are given in detail in Appendix A.

Underdown Chemometrics found that the existing IR - UV/VIS - TRS-80 system did not meet the requirements of the Level 3 concept. The software for data acquisition was too slow to produce data of sufficient quality to identify and quantitate an unknown substance by comparison to the prepared library. Furthermore, the software was not user-friendly. Documentation was determined to be insufficient to allow operation by someone with extensive training in this area. Data often had to be entered several times to perform a single operation, often unnecessarily; at other times the response was redundant based on the answers to previous questions. Some functions, such as PRINT, could not be accessed and/or did not work at all. Other portions of the software appear to be located on Concordia's mainframe which could not be accessed by the contractor and would not prove useful at remote spill locations. Based on these findings it was recommended that the present data handling system be replaced with something more appropriate.

While there are several options available, one of the most expedient routes would be the purchase of pre-packaged software from the manufacturer. Such software is available from Perkin-Elmer, which is compatible with the P-E 3600 Data Station presently used by the gas chromatographic system. In its present configuration the data station will allow interfacing of additional instruments. This data station is based on Motorolla's 6800 8-bit microprocessor. However, with the rapidly moving computer markets, 8-bit micros are giving way to more powerful 16 and 32-bit microprocessors.

One of the most powerful of these new microprocessors is Motorolla's 68000. The Motorolla 68000 microprocessor is the basis of a more advanced data handling system which is now available from Perkin-Elmer; the 36000 Data Station. This data station should offer far greater data handling capabilities and far more versatility than the 3600. Since it is desirable to adopt a system for field use which will not become obsolete soon after the program is established, this new data station should be examined. Should such an investigation reveal that pre-packaged software for this system, does indeed take advantage of the 68000's superior processing ability, this option would

1.0 THE INFRARED (IR) - ULTRAVIOLET (UV) / VISIBLE (VIS) SPECTROPHOTOMETERS - TRS-80 COMPUTER SYSTEM

The Environmental Emergencies Technology Division (EETD) selected the Perkin-Elmer (P-E) Model 683 IR Spectrophotometer and the P-E Model 552 UV/VIS Spectrophotometer as Level 3 compatible systems. Software was developed for these systems by the previous contractor which requires interfacing these intruments to a TRS-80 Mark III computer for data analysis.

The IR system will find greatest application in the analysis of spill site air samples, while the UV/VIS system is expected to be most useful for the analysis of priority substances in the water and soil matrices. These analytical techniques are non-destructive, allowing for subsequent gas chromatographic (GC) analysis of a sample if concurrent analysis is not possible or practical. The UV/VIS and IR systems are envisioned as providing priority chemical identity confirmation capability for substances which are amenable to GC analysis. As supplementary techniques, the UV/VIS and IR systems must have the capability to identify and quantitate substances which cannot be handled by GC techniques.

The features required for the Level 3 UV/VIS and IR computer systems are:

- real-time acquisition of data from the spectrophotometer.
- ability to identify contaminants by comparing sample spectra to a library of laboratory-compiled standard spectra for priority substances.
- quantitation capability once the identity of the priority substance has been determined by the system.
- user-oriented computer software to allow for effective operation of the systems by operators lacking extensive technical backgrounds.

The software and interface, developed by the previous contractor, was evaluated to establish if any or all the above requirements were met, and if not, where improvements could be made. This portion of the work was

sub-contracted to Underdown Chemometrics and the results of this study are given in detail in Appendix A.

Underdown Chemometrics found that the existing IR - UV/VIS - TRS-80 system did not meet the requirements of the Level 3 concept. The software for data acquisition was too slow to produce data of sufficient quality to identify and quantitate an unknown substance by comparison to the prepared library. Furthermore, the software was not user-friendly. Documentation was determined to be insufficient to allow operation by someone with extensive training in this area. Data often had to be entered several times to perform a single operation, often unnecessarily; at other times the response was redundant based on the answers to previous questions. Some functions, such as PRINT, could not be accessed and/or did not work at all. Other portions of the software appear to be located on Concordia's mainframe which could not be accessed by the contractor and would not prove useful at remote spill locations. Based on these findings it was recommended that the present data handling system be replaced with something more appropriate.

While there are several options available, one of the most expedient routes would be the purchase of pre-packaged software from the manufacturer. Such software is available from Perkin-Elmer, which is compatible with the P-E 3600 Data Station presently used by the gas chromatographic system. In its present configuration the data station will allow interfacing of additional instruments. This data station is based on Motorolla's 6800 8-bit microprocessor. However, with the rapidly moving computer markets, 8-bit micros are giving way to more powerful 16 and 32-bit microprocessors.

One of the most powerful of these new microprocessors is Motorolla's 68000. The Motorolla 68000 microprocessor is the basis of a more advanced data handling system which is now available from Perkin-Elmer; the 36000 Data Station. This data station should offer far greater data handling capabilities and far more versatility than the 3600. Since it is desirable to adopt a system for field use which will not become obsolete soon after the program is established, this new data station should be examined. Should such an investigation reveal that pre-packaged software for this system, does indeed take advantage of the 68000's superior processing ability, this option would

be most desirable.

Other computer systems could be used to provide identification and quantitation capabilities but this route would require having specialized software written. While this would provide software tailored to the spill response application, this route would be much more costly.

2.0 THE SIGMA 2000 GAS CHROMATOGRAPH (GC) - 3600 DATA STATION

General Description

The Perkin-Elmer Sigma 2000 gas chromatograph and the 3600 data station were chosen by EETD to provide analytical capability for a large number of the Priority Hazardous Substances under the Level 3 concept.

The Sigma 2000 GC is a microprocessor-controlled instrument. Its modular design provides convenient access to various components for ease of maintenance, repair and modification. In its present configuration the gas chromatograph can be used with the following injection systems:

- a standard heated flash vaporizing injector.
- a split/splitless injector (for capillary use).
- a manually operated heated gas sampling valve.
- an HS-6 Head Space analyzer.

While several detector options are available, the instrument is presently configured to take advantage of the system's dual acquisition capability. This arrangement passes the column effluent through a photoionization detector (PID) into a flame ionization detector (FID),thus allowing the detection of eluting compounds by the PID - a non-destructive detector - before detection by the FID - a more universal detector for organics. Thus two sets of information can be obtained for many organic compounds such as alkenes and aromatics.

Another detecctor - the Electron Capture Detector (ECD) - has also been purchased by EETD. However with the extreme sensitivity of this detector to its environment and its very low detection limit, this detector is not likely to be useful for field applications. Furthermore, only two detectors can be installed on the GC at once. Other detector systems are also available, some of which will be discussed later.

The Sigma 2000 is interfaced to the P-E Model 3600 Data Station which is capable of real-time acquisition and post-run data manipulation. This data

station is linked to the Sigma 2000 through a P-E interface box, which makes simultaneous dual acquisition possible. This contract work has also provided software to build and use a laboratory-compiled database for compound identification and quantitation.

2.1 INJECTORS

The injectors for the Sigma 2000 are located at the left, front of the instrument and are contained in interchangeable cylindrical modules. The injector heater connections are made via sockets mounted at the front of the oven (see Figure 1).

Several types of injection systems are available for the gas chromatograph. The selection of an appropriate injection technique is based upon the medium being analyzed, the nature of the compounds of interest and the type of chromatographic column being employed. Each of the following types of injector techniques will be described briefly.

- Heated Flash Vaporization
- Split/Splitless Injectors
- Gas Sampling
- Head Space Analysis

2.1.1 Heated Flash Vaporization

Heated Flash Vaporization injection is likely the most common injection technique used when analytical separation is done with packed columns. This technique involves introduction of the sample into a heated injector body by inserting the stylus of a syringe through the septum at the head of the injector. The sample is vaporized in the heated injector body and swept onto the front of a chhromatographic column by the carrier gas (See Figure 2). Sample volumes of 1 to 10 uL of liquid are common with this technique. Larger volumes of gas samples may be injected using gas sampling syringes.

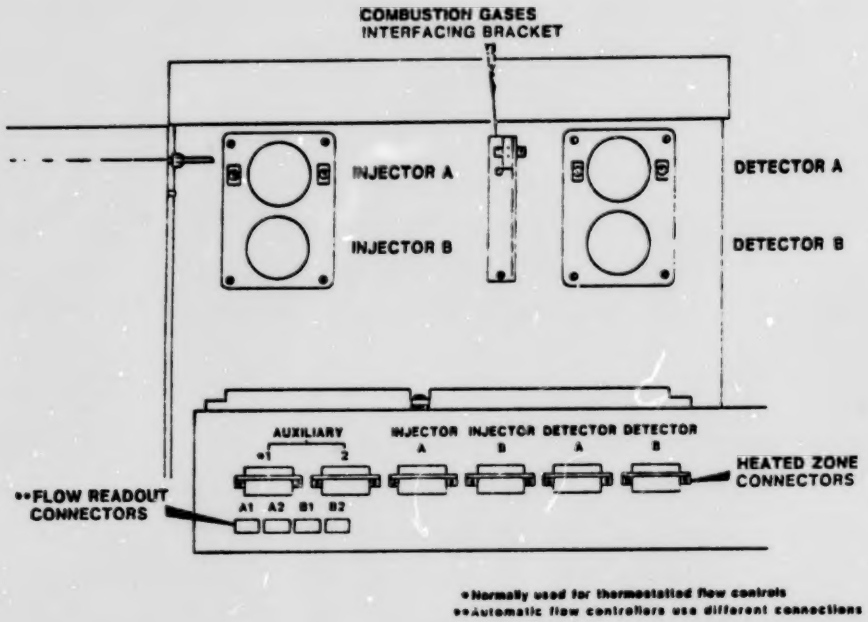


Figure 1 - Heated Zone and Flow Readout Connectors For Injectors and Detectors

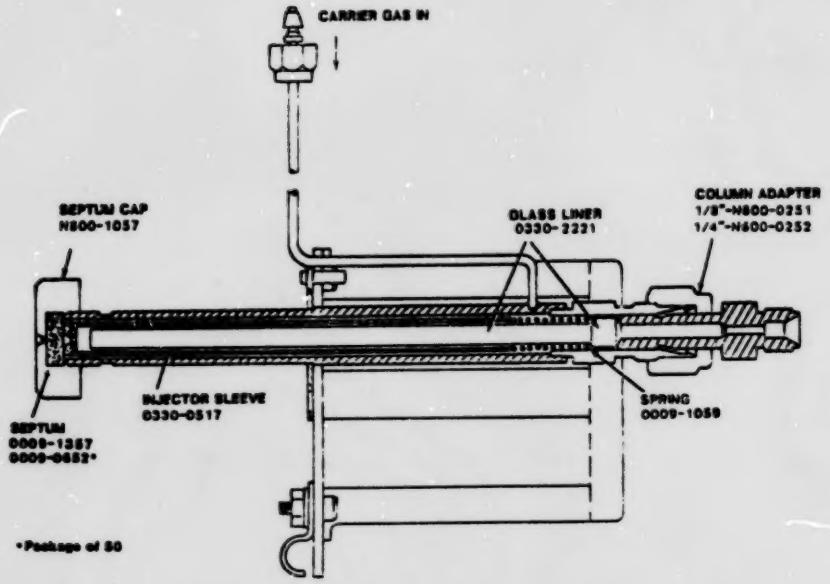


Figure 2 - Heated Flash Vaporizing Injector With 1/8-in. or 1/4-in. Column Adaptor

2.1.2 Split/Splitless Injectors

The split/splitless injection technique is usually employed when small amounts of contaminants are analyzed using capillary columns. Since capillary columns have a much smaller internal capacity than packed columns, smaller sample volumes are required. To accommodate these small volumes the split/splitless injector (Figure 3) has been designed to operate in two different modes, the selection of which depends on the nature of the sample.

The split mode allows the introduction of a small portion of the injected sample onto the head of a capillary column with the remaining portion being vented. The size of the sample being introduced onto the column is controlled by the "split ratio" or the ratio of carrier gas being passed through the column to the amount which is being vented. The glass liner in the heated injector body is packed with glass wool or a chromatographic packing material in an attempt to 'split-off' a larger portion of the solvent than the compounds of interest.

The splitless mode is used for trace analysis where it is desirable to further concentrate the sample extract and minimize the amount of solvent passing through the column. As with the split mode, the sample is introduced into a heated injector body. However, in the splitless mode all vents are closed during the injection period. The internal bore of the glass liner is usually smaller than that for split and it contains no packing material. The vaporized sample is swept onto the head of the chromatographic column by carrier gas while maintaining the column at 20 to 50C below the boiling point of the solvent (usually the lowest boiling compound in the sample). Some of the solvent and most of the trace components are condensed at the head of the column, thus concentrating and focussing the sample constituents into narrow bands. After an appropriate period of time, usually 20 to 60 seconds, the split vent and septum purge valves are opened to flush the residual solvent from the injector body. At this time, or soon after, the chromatographic column is temperature programmed to give appropriate separation of the components. The advantages of such a focussing and concentrating technique are clearly seen in Figure 4.

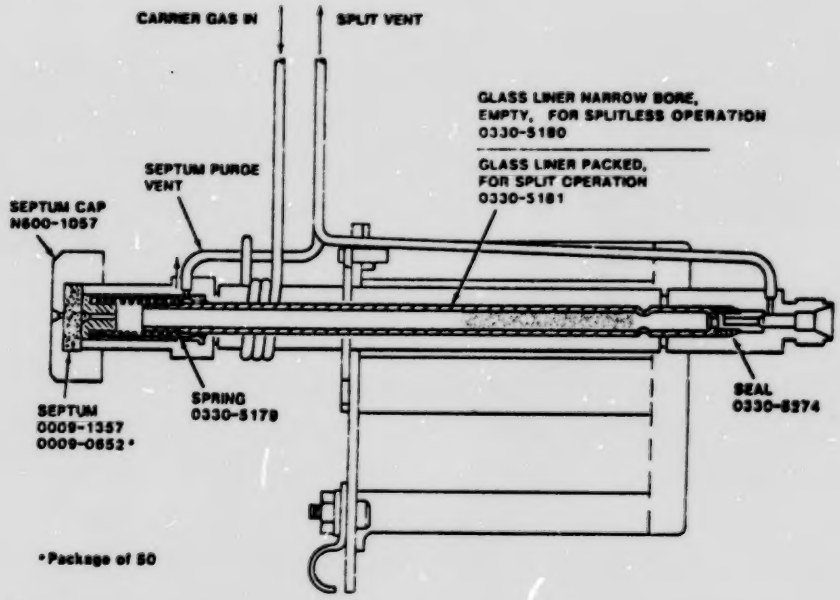


Figure 3 - Split/Splitless Injector

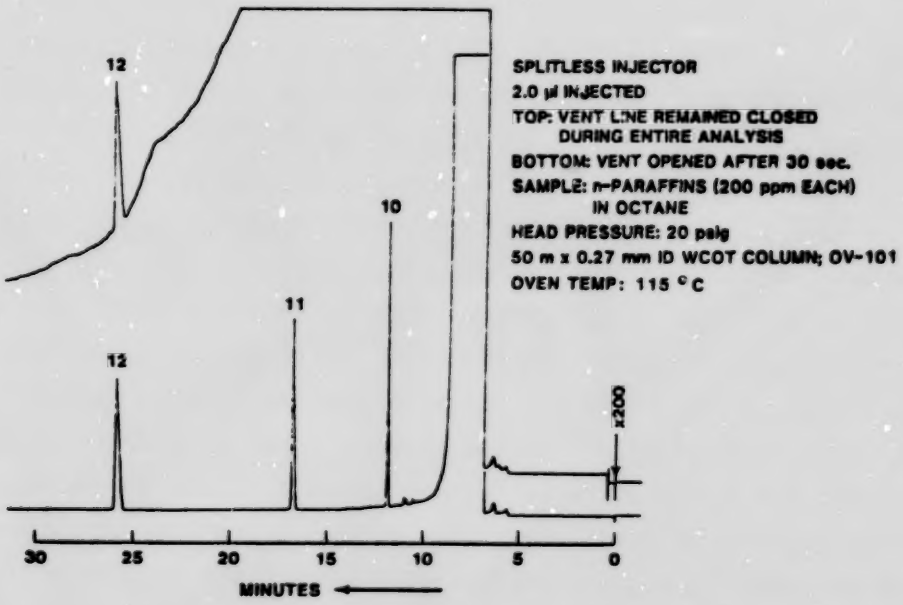


Figure 4 - Conventional vs. Splitless Injection

Injection volumes typically range from 0.1 to 5 uL with smaller volumes (ie. 1 uL) being preferred. Larger injection volumes decrease resolution and degrade peak shape. Furthermore, the chromatographic capacity of the column is often exceeded if large volumes are used.

2.1.3 Gas Sampling Valve

This method of injection allows the introduction of a gas sample onto the head of a chromatographic column. The technique involves filling a 'loop' of a fixed volume (usually 0.1 to 10 mL) with a gaseous sample. The sample 'loop' is then allowed to equilibrate to atmospheric pressure before the valve position is rotated, re-routing the carrier gas through the loop into the column. In this orientation, the sample is swept onto the head of the column, which is maintained at a temperature selected to provide adequate focusing of the sample constituents. Both the temperature and pressure of the sampling loop must be maintained constant to ensure that a reproducible sample volume is injected. Since large volumes of gas are required to achieve 'reasonable' detection limits for trace analysis, packed columns are usually employed. If the higher resolving capability of capillary columns is required, modifications must be made to concentrate the sample and reduce the volume of gas required to transfer the sample.

2.1.4 Head Space Analysis

Head space analysis is not strictly an injection technique. It allows the extraction of trace amounts of volatile organics from aqueous and solid media prior to injection on a chromographic column. The technique is most appropriate for media where one wishes to analyze compounds which have relatively high vapour pressures in samples with a high non-volatile content.

The head space analysis technique involves placing the sample material in a hermetically sealed sample vial, heating the vial to a specified temperature and allowing equilibration of the volatile fraction in the sample with the gaseous phase above the sample. Once equilibrated, a portion of the gaseous phase is withdrawn and delivered to the head of a chromatographic column or pre-column (Figure 5).

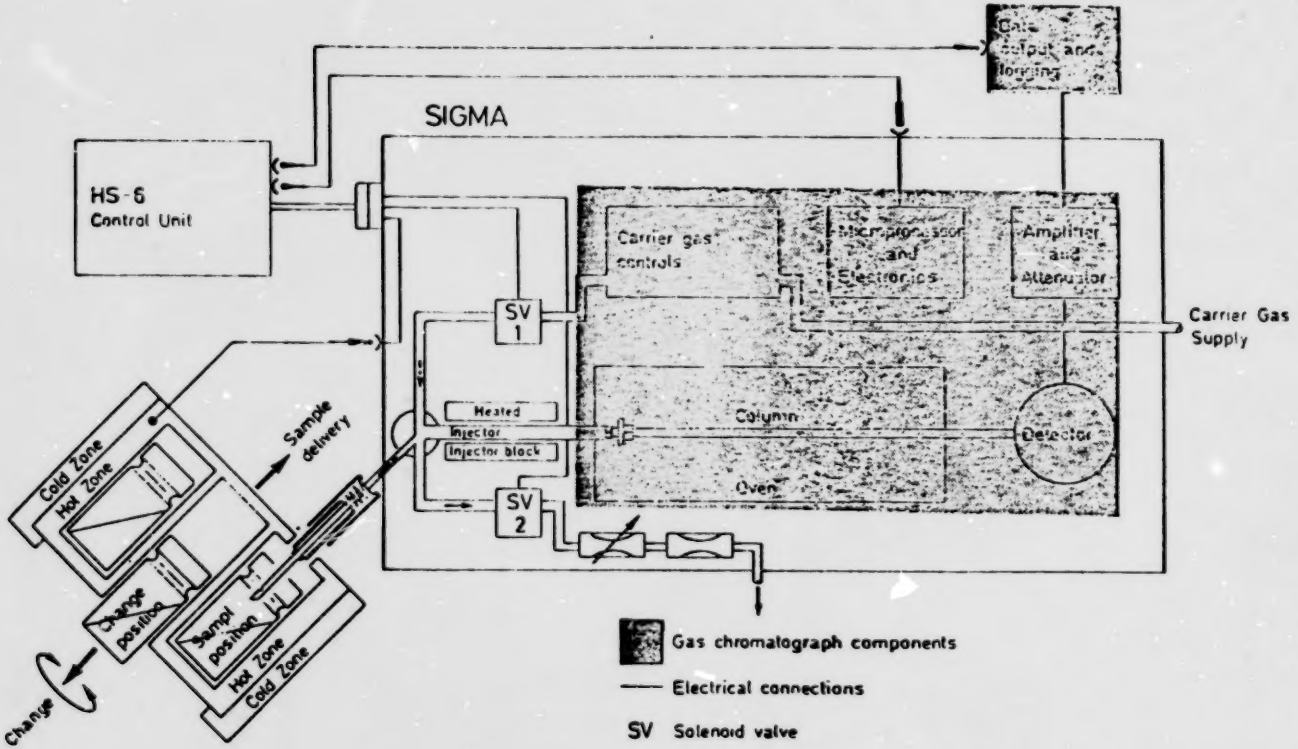


Figure 5 - Operational Diagram of the Model HS 6 with a SIGMA Series Gas Chromatograph

The HS-6 head space analyzer installed on the Sigma 2000 GC is semi-automated thus allowing for heating and equilibration of a maximum of six samples at one time. Injection and rotation of vials must be manually initiated.

Injection of the 'head space' is achieved by pressurizing the equilibrated vial, thus forcing a portion of the gas through the sampling needle onto the head of the column. The size of the sample is determined by the pressurization time. This technique does not quantitatively transfer the volatile fraction but analyzes a reproducible fraction of the components, which is based on the partitioning of the organics between the gaseous and aqueous or solid samples. Standards run under identical conditions allow for accurate quantitation of the components of interest. Again since large volumes are injected, appropriate modifications must be made before the technique can be used with capillary columns.

2.2 DETECTORS

Detectors, like the injectors, are mounted on the Sigma 2000 GC in interchangeable cylindrical modules at the right, front of the GC oven and are connected to heaters and control boards via sockets mounted at the front of the oven (Figure 1). A brief description of the following detectors is presented.

1. Flame ionization detector (FID)
2. Photoionization detector (PID)
3. Electron capture detector (ECD)
4. Hot Wire detector (HWD)

2.2.1 Flame Ionization Detector (FID)

The flame ionization detector is one of the most universal detectors for organics since it is designed to detect the positively-charged carbon particles that are formed when organic molecules are burned in a hydrogen flame. These charged particles are forced to migrate toward the collector electrode by a polarizing electric field. The current produced at the

collector electrode by the charged particles is proportional to the amount of compound present, thus allowing quantitation. The simplicity of design makes the FID one of the most stable and easily operable GC detectors. In addition, it exhibits low sensitivity to its environment, making it suitable for field applications. Maintenance of the FID is minimal and includes occasional cleaning or replacement of the jet. The frequency of required maintenance is dependent upon the type of columns being used and types of compounds being analyzed. With use of low bleed columns and non-corrosive compounds the FID may need no maintenance for several years. Details of the maintenance procedures are given in Section 8 of the P-E GC Instruction Manual (Part no. 0993-9787). See Figure 6.

2.2.2 Photoionization Detector (PID)

The PID design is based on detection of ions produced when a molecule absorbs photons, ie:

$$R + h\upsilon \longrightarrow R^{+} + e^{-}$$

where R is the ionizable species. The ability of the detector to ionize species is dependent upon the energy of the photon being emitted by the UV source and the ionization potential of a particular compound. The PID is capable of detecting some inorganic compounds as well as many organics. The PID is more selective than the FID since it does not respond to compounds with ionization potentials greater than that of the UV source (ie. 10.2 eV). In addition, the PID is far more ssensitive than the FID for certain compounds (ie. alkenes, aromatics). Since the PID is a non-destructive detector it can be used in series with other detectors such as the FID. See Figure 7.

While the design of the PID makes it more sensitive to some compounds, it also makes the detector more sensitive to its environment. The performance of the detector is dependent on the use of high-purity gases and well-conditioned, low-bleed columns. The presence of water or oxygen can adversely affect the performance of the detector. Furthermore, the flow rate of the carrier gas past the UV window influences stability and thus must be carefully controlled. The detector requires routine maintenance, which includes cleaning the UV lamp

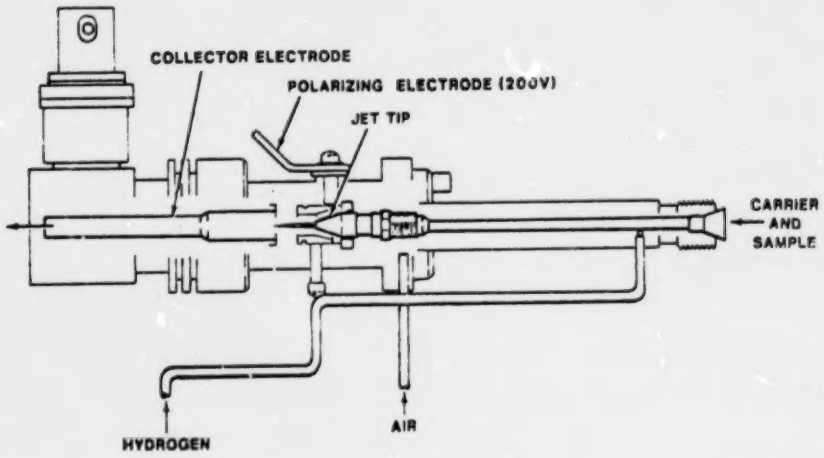


Figure 6 - Flame Ionization Detector

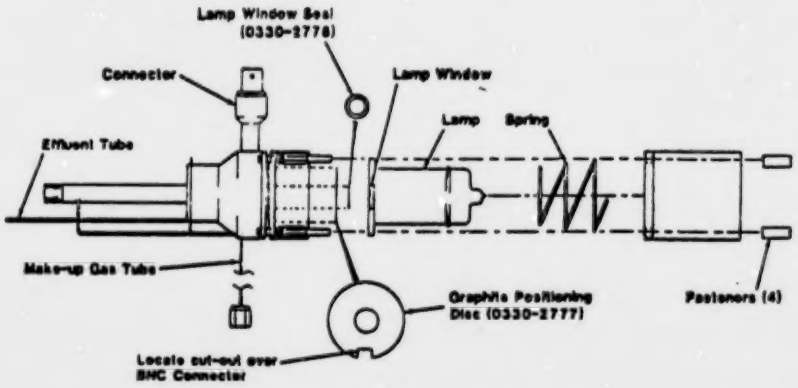


Figure 7 - Exploded Diagram of Photoionization Detector

window, changing the lamp, replacing the lamp window seal and replacing the graphite positioning disc (see Section 4 of Perkin-Elmer Manual 0993-9846). The frequency of such maintenance is dependent on the type of compounds being analyzed and is indicated by the loss of sensitivity. The performance of the PID in field situations is not known. However, due to its high sensitivity to its environment, problems are anticipated.

2.2.3 Electron Capture Detector (ECD)

The ECD detector is very sensitive to compounds which easily absorb electrons such as halogenated organics. The detector contains a radioactive foil source, usually Nickel 63, which emits negative beta particles. A polarizing electric field is used to set up a constant current to the anode. When an electron absorbing species passes through the cell, the current decreases an amount corresponding to the concentration of electrophyllic species present. Thus to maintain a constant current, the closed-loop circuit must increase the polarizing pulse frequency accordingly. The change in frequency is detected, amplified and recorded to give quantitative analysis of the compound passing through the cell (see Figure 8). The cell volume is sufficiently large that 'make-up' gases must be used to obtain acceptable peak shape. The ECD detector, like the PID is a non-destructive detector and is extremely sensitive to its environment. The detector must be stabilized for a minimum of 24 hours before reproducible results can be obtained, even with changes in operating temperatures. The detector is also very easily contaminated, which is indicated by a drastic slope change in the standing current curve. The cleaning and maintenance procedure is described in Section 8A of the GC Instruction Manual.

2.2.4 Hot Wire Detector (HWD)

The HWD is a non-destructive dual channel detector which measures the difference in thermal conductivity between the reference gas stream and the sample gas stream. This detector responds to all compounds whose thermal conductivity is different from that of the carrier gas. A schematic of the HWD is given in Figure 9. The detection circuit is essentially a wheatstone bridge which is forced 'out-of-balance' when conducting compounds pass by the

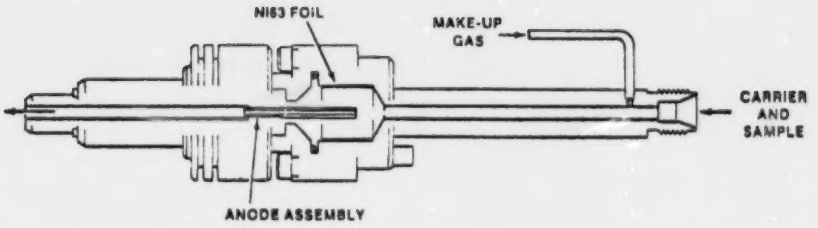


Figure 8 - Electron Capture Detector (ECD)

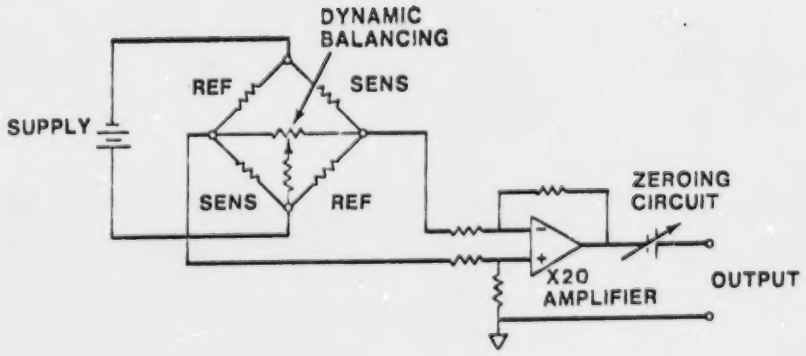


Figure 9 - Hot Wire Detector

filament in the sample chamber. The HWD requires very little routine maintenance and stabilizes quickly, making it suitable for field use. The tungsten - rhenium filaments are somewhat sensitive to oxygen and as such should not be powered when exposed to air. The HWD can reliably detect compounds over a large range of concentrations, a desirable feature for spill response applications. Furthermore, response factors for most organics do not vary extensively as the detector is not group specific. The HWD is not capable of the low detection limits of many of the other detectors but will see 1 to 10 ppm of most compounds, making it a viable option for on-site spill reponse applications.

2.3 GAS CHROMATOGRAPHIC COLUMNS

The proper selection of a chromatographic column is a major determining factor in the success of the analytical technique. The column must be capable of adequately separating all the compounds of interest such that only one compound enters the detector at a time, allowing for accurate quantitation. The selection of such a column for the purposes of this study is further complicated by the requirement for the column to endure field use and yet maintain sufficient stability to allow quantitation of a wide variety of organics, without the availability of analytical standards. Thus, the following characteristics must be considered when choosing appropriate columns:

- The resolving power of the column for a wide variety of compounds.(ie. minimize the number of columns and thus the number of compound libraries required in the field.)

- The stability of the column. If laboratory-compiled databases are to be used for identification and quantitation then changes in retention times and response must be minimized.

- The compatibility of the column with injection and detection techniques.

- The physical characteristics (ie. will it survive under field

conditions?)

Unfortunately, no one column will meet all the above requirements for all the organic compounds on the Priority Hazardous Substances list (Appendix B).

To address the resolution requirements of many of these substances, the choice of a bonded-phase fused silica capillary column (ie DB-5) would be most desirable. However, many of the more volatile organics cannot be adequately separated on these columns without the use of cryogenic focussing, an option which may be difficult to adapt to field use. Furthermore, the low internal volume of these columns makes direct interfacing with gas sampling and head space sampling techniques impossible without the addition of appropriate concentration and focussing techniques. Time and funding did not allow for these modifications in the first phase of this project. Additional problems associated with the use of capillary columns with the Level 3 concept include:

- The low 'loading' capacity of capillaries thus requiring dilution of heavily contaminated samples; a task which may not be easily accomplished in the field.

- Low flow rates of carrier gas through the column thus requiring 'make-up' gases to the detectors and making reliable effluent splitting across two detectors very difficult.

- Column fragility - making transportation and installation more complex.

- The cost - greater than $500.00 Cdn. per column.

Thus it was decided that packed columns would be used for analytical separation, at least for the initial stages in the development of the concept. Since contaminants in air were deemed to be of highest priority, the initial work addresses the more volatile liquids on the priority list.

The chromatographic column selected for separation of a large portion of these compounds was a 6ft. x 1/8in. stainless steel column packed with 1% SP-1000 on 60/80 Carbopack B. Previous experience with this column indicated that it was

a good general purpose column for low-boiling organics and that it exhibited good stability over long periods of time. In addition, its low bleed characteristics would allow its use with the PID detector.

2.4 3600 DATA STATION

As indicated earlier, the Sigma 2000 gas chromatograph is interfaced with the Perkin-Elmer Model 3600 Data Station. The interface of the two instruments is achieved via an RS-232 auto-switch and a microprocessor-controlled synchronous dual-channel interface box which converts the analog data from the GC to digital data for use by the data station. The data station allows real-time plotting of the chromatograms on the VDU and allow the user real-time control of display attenuation and time scale. Pre-run defined parameters allows control of screen display (ie. split-screen for multiplex mode), size of full screen display (in mV), data acquisition rate and the type of data stored (ie. raw data and/or report form). The data system is equipped with two disc drives. During operation the left drive (0) must contain the chromatography control software and methods. Raw data is sequentially stored in real time on the right drive (1). The size of data files is based upon method defined parameters, such as minimum peak width and is pre-determined by the data system. If insufficient disc space is available the data system will not initiate a chromatographic run.

Two versions of the chromatographic software have been provided by Perkin-Elmer. One version contains just acquisition and post-run manipulation software, the second contains GC communications software in addition. The software is presented in this way because the communications software version is very large, thus leaving minimal space for method storage (a maximum of three methods). The CHROM software requires that methods be stored on drive 0, and uses some space on this disc during operation. For these reasons, the software version without communications capability has proven to be most useful for this study.

2.5 LABORATORY-COMPILED DATABASE

To allow identification and quantitation of priority organics in the field, without the availability of analytical standards, it is desirable to have the necessary information in the form of a database. However, the construction of a reliable database is not straightforward, as changes in retention times and response of the detectors are not unlikely, especially in a field situation. The use of an external standard was adopted, in an attempt to compensate for changes in retention time and response, against which a database could be constructed which used relative retention times and responses as a basis for identification and quantitation. In addition, certain criteria will be established based on the response of this standard, outside of which the performance of the GC would be considered unreliable.

2.5.1 Software

Since no software was available which would address these requirements, Underdown Chemometrics was contracted to develop software which would allow the identification of an unknown by relative retention time to the external standard and quantitation of the same via relative response to the standard. The software developed to meet these requirements is outlined in detail in Appendix C. This software allows the creation of a random access library file containing the following information:

- The compound name
- The library number (sequentially stored)
- The PID retention time (relative to external standard)
- The FID retention time (relative to external standard)
- The ratio of PID/FID response
- The PID response factor (relative to external standard)
- The FID response factor (relative to external standard)

In its present configuration, a maximum of two hundred compounds can be stored per library. Any number of libraries can be created but must be stored on different discs under the file name MLIB1.

External standard retention times and areas for both detectors (PID/FID) must be manually entered. However, sample data is read directly from report files created by the CHROM 2 software. The menu-based library comparison software will identify and quantitate individual peaks in a multicomponent mixture and allow the user to define portions of the chromatograms for analysis. This feature eliminates unnecessary analysis of peaks. Results of the database comparisons are reported as the five 'best fits' based on retention time matches, with the difference in retention time between the unknown and the library entry also being reported. In addition, the amount of each of the five 'best fits' is calculated based on stored response factors. Information from each detector (PID and FID) can be analyzed separately and/or in conjunction with the calculation of the difference in relative response of the PID and FID, for each of the five closest library matches against similar data for the library entry. This feature allows a second confirmation technique for compounds responding to both detectors.

2.5.2 Database Development

Since contaminants in air were deemed to be of greatest concern, the development of a library to address these compounds was a first priority. It was also desirable to evaluate the performance of the various injection techniques. The first step was to obtain results from direct injection onto the chromatographic column (ie. heated flash vaporization injector). With this information at hand it would then be possible to evaluate the performance of the gas sampling valves and head space sampler for these 'low boiling' organics. A library compiling this information relative to a constant amount of an external standard would further simplify and optimize later stages of the development work.

Benzene was selected as the external standard for this group of compounds since it chromatographs approximately mid-way between the first and last compounds being addressed (ie. approximately 20 minutes) and responds well to both detectors.

Data for the library was obtained by running individual compounds on the gas chromatograph, using the heated flash vaporization injector, at a variety of concentrations to establish retention times, response to both detectors (PID and FID), linearity of the detectors over a range of concentrations and to obtain some indication of the lower detection limits. This detection limit would not necessarily be the lowest possible detectable amount but the lowest amount reliably and routinely detected in the GC's present configuration.

Calibration data is provided in Appendix D for all compounds analyzed to date. The database has been compiled using average retention times and areas based on the results of least squares analysis. Data for several compounds was found to be non-linear for one or both detectors and as such cannot be used for quantitation purposes. These compounds have not been entered into the library. Response factors used for the database have been calculated from regression analysis data. This information is tabulated in Appendix D (D-1) and the database is stored on the diskette labelled DATABASE 1.

2.6 OPERATION OF GAS CHROMATOGRAPH (GC) AND DATA STATION

The Sigma 2000 GC can be controlled from the keypad incorporated at the right of the GC or from the data station using the CHROM 2 software with communications. The communications software is menu-controlled and is basically self-explanatory. Details are given is Section 13 of the Chromatographics 2 Instruction Manual. Since this version of the software was not used in the study, for reasons explained earlier, the description provided will be based upon use of the GC keypad.

Data acquisition, likewise is controlled by methods created and stored on the 3600 data station. The manipulation of such information will be outlined in the ensuing sections. Daily start-up and shutdown procedures will also be discussed.

2.6.1 Generation of a GC Method

GC control is divided into two types of functions; the sections which are accessible at all times and the systems which are less frequently used. A detailed description of the sections and systems is given in sections 3 and 4 of the GC Instruction Manual and thus will not be repeated.

Briefly, the major sections are:

Section 1 - Instrument Status
Section 2 - Active Method
Section 3 - Method Control

Section 1 is divided into two pages, the first of which displays information of interest during a run (ie. runtime, oven temperature, etc.) and allows zeroing of the detectors. The second page displays a list of NOT READY devices indicating zones which deviate from the set value.

Section 2 displays the parameters in the method that is controlling the GC, such as maximum oven temperature, injector and detector temperature, flow rates, temperature parameters, and timed events. This section is divided into three pages which can be accessed by pressing the <ADV> key and entering the appropriate page number.

Section 3, unlike the other two sections, is menu-based and allows manipulation of method files. In this mode one can select one of seven operations to generate/edit, delete, copy or store a method. In addition, it allows the user to change the method controlling the GC to one of the other stored methods.

For the purposes of this study, the parameters required for operation of the GC are provided in Method 3, see next page. Method 1 provides column conditioning and overnight bake-out parameters. See next page.

All the systems are menu-accessed. Default parameters are provided in each system, however, some must be altered to operate the GC in its present

configuration. The system functions are:

1. Run deviations
2. Inj/flow change
3. Detector change
4. Instr change
5. Misc functions
6. Print page
7. Set Time/Date
8. Stopwatch display
9. Clock running
10. Error status
11. Comm. options
12. Keyboard lockout

The only systems which must be altered for operation are 2, 3, 7 and 11. In system 2, the subambient function should read 'OUT'. This value is changed by moving the cursor to the appropriate position and entering -1.

System 3 should read: CHAN: A FID
CHAN: B FID

This is done by moving the cursor to the appropriate lines and entering the number 6. The detector on channel A is actually a PID but there is no PID option, furthermore, the electronics for both detectors are the same.

System 7 sets up an internal clock and thus the time and date must be entered.

System 11 controls communication with external devices. To link the 3600 data station to the GC, the baud rate must be changed to 9600 and the PROMPT MSG default value of 17 must be removed, by moving the cursor to this line and entering the number 255 (the code to delete a decimal ASCII Character) See Section 2 paragraphs 64 to 68 in the Chrom 2 Instruction Manual.

INSTRUMENT CONTROL. INST# 1 SIGMA 2000

PRINT METHOD FROM SIGMA 2000 METHOD 1

GE 1 OF 3 TEMPERATURE PROGRAM

	1	2	3	4
OVEN TEMP	150			
TIME	INF			
RATE				

FLOWS	SET
A1	
A2	
B1	
B2	

ZONES	SET
INJ A	250
DET A	250
INJ B	OFF
DET B	250
AUX 1	OFF
AUX 2	

PAGE 2 OF 3 INITIAL VALUES

OVEN MAXIMUM TEMPERATURE 250 EQUILIBRATION TIME 0.5
CHANNEL A FID RANGE 1 CHANNEL B FID RANGE 1

INSTRUMENT CONTROL. INST# 1 SIGMA 2000

PRINT METHOD FROM SIGMA 2000 METHOD 1

PAGE 3 OF 3 RUN TIMED EVENTS

TIME	EVENT	VALUE

INSTRUMENT CONTROL. INST# 1 SIGMA 2000

PRINT METHOD FROM SIGMA 2000 METHOD 3

PAGE 1 OF 3 TEMPERATURE PROGRAM

	1	2	3	4
OVEN TEMP	65	100	200	
TIME	4.0	0.0	35.0	
RATE	4.0	8.0	0	

FLOWS	SET
A1	
A2	
B1	
B2	

ZONES	SET
INJ A	250
DET A	250
INJ B	OFF
DET B	250
AUX 1	OFF
AUX 2	

PAGE 2 OF 3 INITIAL VALUES

OVEN MAXIMUM TEMPERATURE 250 EQUILIBRATION TIME 0.5
CHANNEL A FID RANGE 1 CHANNEL B FID RANG

INSTRUMENT CONTROL. INST# 1 SIGMA 2000

PRINT METHOD FROM SIGMA 2000 METHOD 3

PAGE 3 OF 3 RUN TIMED EVENTS

TIME	EVENT	VALUE

Changes to systems 1, 5, 8 and 10 are optional. System 1 indicates deviations of actual parameters from the defined parameters during a given run.

System 10 indicates the source and type of error should one occur. This mode is often used when troubleshooting; section 8B of the Sigma 2000 instruction manual lists error codes and their meaning.

System 5 will allow activation or deactivation of the KEYSTROKE BEEPER.

System 8 accesses a stopwatch.

Systems 4, 6, 9 and 12 need not be altered under normal operating conditions.

2.6.2 Generation of a Data Handling Method

The CHROM software requires the generation of a 'method' to control data acquisition and post-run manipulations. Since explanation of the various parameters would be rather lengthy and has already been discussed in the Chromatographics 2 Instruction Manual, this section will only present the method required for operation of the GC system in its present configuration. The method 'ABC' was developed to address the low-boiling compounds discussed earlier. A copy of ABC follows. Once in the method section, the data system will prompt the user to enter the required parameters. The only parameters which need be altered from run to run are:

1. The sample description
2. The data acquisition start time
3. The data acquisition end time.
4. The 'disc file prefix' - the name of the file(s) which the data will be stored under. PID data files should start with PS and FID data files should start with FS.
5. Printed plot min/page - should be adjusted to correspond with the end time of the run.

******** METHOD ABC ********

DATA ACQUISITION PARAMETERS	
INTERFACE NUMBER	1
DATA CHANNEL	M
DATA START TIME IN MINS.	0.0
DATA END TIME IN MINS.	30.0
PEAK DETECTION THRESHOLD	0.80
MINIMUM PEAK WIDTH IN SECS.	10.0
DISPLAY AND STORE DATA DURING RUN	Y
TIMED EVENTS TABLE REQUIRED	N
MORE DATA PROCESSING PAGES	Y
CALCULATION PARAMETERS	
CALIBRATION BY AREA/HEIGHT	A
SKIM FACTOR	5
CONCENTRATION UNITS	
REPORT GENERATION	
AREA/HEIGHT PERCENT	Y
NORMALISED PERCENT	N
EXTERNAL STANDARD	N
INTERNAL STANDARD	N
GROUPED REPORT	N
RETENTION TIME WINDOWS	
PERCENT	5
FIXED	5
SAVE DATA	
PLOT FILES	Y
REPORT FILES	Y
PRINT PLOT	Y
NUMBER OF RUNS	1
CHANNEL A	
SCREEN FULL SCALE MV	1000
AREA REJECTION	100
DISC FILE PREFIX	PS
PRINTED PLOT MIN/PAGE	30
VERTICAL SCALE FACTOR	1
CHANNEL B	
SCREEN FULL SCALE MV	1000
AREA REJECTION	100
DISC FILE PREFIX	FS
PRINTED PLOT MIN/PAGE	30
VERTICAL SCALE FACTOR	1

2.6.3 Instrumentation Set-up

Cold Start

1. Turn on carrier gas (He) - tank pressure should be adjusted to 90 psi on the second stage of the regulator.

2. Make sure the proper column is installed and that 30 mL/min of carrier is passing through the column.

3. Check that the column effluent is passed through the PID and into the FID.

4. Turn the POWER on at the front of the GC and the STANDBY on at the back panel to charge the battery back up.

5. Enter methods 1 and 3 into GC memory from keypad using section 3 and make required changes to system parameters. See section 2.6.1.

6. Define Method 1 as the setup method (section 3) and condition the column for several hours (if the column has not been previously conditioned do not connect it to the detectors and follow manufacturer recommended conditioning procedures.)

Warm Start

7. Turn on Hydrogen and Air cylinders.
   Hydrogen tank - 40 to 50 psi
   Air tank - 40 to 50 psi
   Air / Hydrogen pressure regulators, located at the bottom left hand side of GC should be set as follows:

   Air (yellow) - 5psi
   Hydrogen (red) - 20 psi

8. Turn on power to the PID and allow to warm-up for approximately 30 minutes.

9. Go to GC section 3 and change the control method to method 3 and allow the oven to cool down and stabilize.

10. Light the FID:
    - wait approximately 15 minutes from time the air and hydrogen cylinders were turned on, to allow the gases time to reach the detector.

    - Hold igniter over the end of the FID and press in firmly.

    - Slowly turn air pressure up to 20 psi - you may hear a 'pop'.

    - Hold a shiny surface over the end of the FID to check for condensation (ie. flame lit). If unsuccessful turn down air pressure to 5 psi - wait a few minutes and try again.

    - You may have to make several attempts before the flame lights. Two things which may help if unsuccessful after several tries:

1. Remove clip at end of FID
2. Increase Hydrogen pressure slightly to light flame and then reduce to 20 psi.

11. Turn on PID lamp and turn the lamp intensity to the 12 o'clock position.

12. Wait for oven and detectors to stabilize.

Using Data System

13. Turn on interface box

14. Turn on the autoswitch

15. Place CHROM 2 disc (disc labelled CHROM 2 Rev C OPERATING, copy) in Drive 0 (left) and data disc (disc labelled Database 1 or a blank formatted disc,) in Drive 1 (right)
    Note: The heads on the disc drives will start spinning as soon as the disc is introduced and will continue to spin unless they are not accessed. The LED on the front of the drive only indicates when the disc is being accessed. Caution must be exercised when removing or introducing discs. It is possible to damage discs on the spinning head.

16. Turn on data station

17. Enter time and date as prompted; the system should then respond with PETOS >

18. Load the chromatography package by typing CHROM <return>
    The system will then ask for:
    THE TYPE OF INSTRUMENT ON PORT B.
    Press <Return>

    The system will respond:

CIT2> READY FOR NEXT COMMAND

You have now entered the chromatography software routine.

19. Check to see if the data processing method is on disc 0 by pressing

    <METHOD DIRECTORY>

    a blue special function key at the top left hand section of the keyboard. The method of interest for the volatiles is 'ABC' - airborne contaminants. See section 2.6.2.

20. Initiate the data acquisition sequence by pressing the special function key marked <METHOD>
    The system will prompt:

    METHOD IDENTIFICATION
    NAME [DATA FILE NAME]

    Type ABC return, then press the <ACCEPT> key (shift method)

    The system will prompt
    MODIFY METHOD [Y OR N]?
    unless the method is known to contain all the desired parameters respond Y, which enters the first page of the method file. The method file should contain the parameters described in section 2.6.2. Sample descriptions, start and end times, and file names can be changed to be compatible with the samples being analyzed. Movement to the next page is achieved by pressing the <ACCEPT> key. The cursor position can be changed within a page using the arrows (↑↓) keys at the right of the keyboard.

    After the last page of the method, the system wiill prompt:
    OVERWRITE METHOD ABC [Y OR N]?
    To store the changes made previously enter Y. If you enter N it will allow you to enter another Method Name

to store the information under but will not allow you access to the method pages.

21. The system will then prompt:
    INITIALIZE INTERFACE 1 [Y/N]?
    To start a data run enter Y

    The data system will set up the VDU display and prompt:
    PRESS START ON INTERFACE 1 AT INJECTION
    This is unnecessary as the interface start is triggered when the GC start button is pressed.
    The three LEDs on the interface box should be illuminated at this point.

22. If the GC is ready (ie. READY light on) then a sample can be injected

Manual sample injection (Heated Flash Vaporization)

23. Withdraw 1.0 uL of the sample using a 5.0 uL syringe - check that there are no bubbles in the syringe.

    Insert the stylus of the syringe through the injector septum and then rapidly push in the plunger. Immediately press the START button on the GC. This will initiate data acquisition. The data will automatically be stored on Drive 1.

24. At the end of a run, a report and plot will automatically be printed. Once these have been printed the system will prompt:
    INITIALIZE INTERFACE [Y/N]?
    If you wish to do another run respond Y.
    If no, enter N and you will be returned to CIT2>

25. To exit the chromatography software push the <SYS> key, lower right hand side of keyboard. This will return you to PETOS>

2.6.4 Using Database

To access the database, return to PETOS> using the <SYS> key
e.g. CIT2> <SYS>

1. Clear memory
   PETOS> CA <Ret>

2. Check that the library (Database 1) and the desired data files are on drive 1
   PETOS> DIR MFD1: <Ret>

3. Check that the library comparison file (COMP1) and the BASIC software are on drive 0
   PETOS> DIR MFD0: <Ret>

4. Then clear memory
   PETOS> CA <Ret>

5. Allocate additional memory space
   PETOS> BASIC/20 <Ret>

6. Load the comparison program
   BASIC> LOAD "MFD0: COMP1.BA" <Ret>

7. Start the comparison program
   BASIC> RUN <Ret>

The program will prompt you for the names of the FID and PID report files containing the results for the unknown sample. Then it will ask for retention times and peak areas for the benzene standard. Once this information has been entered the system will ask for the earliest and latest peaks to be processed. If there are some differences in the number of peaks within the subset (ie no PID response) then the system will inform you.

The COMP1 program will then provide you with a menu to allow you to select the type of analysis you wish to do. When the library comparisons are completed enter the number 5 and the program will return you to BASIC. At this point hit the <SYS> key to return to PETOS>. For further details see appendix C.

2.6.5 Instrumentation Shutdown

1. Turn LAMP and POWER to PID off

2. Cool oven temperature to 50°C and then change the septum in the injector

3. Change the GC control method to Method 1. (from Section 3)

4. Turn off hydrogen and air at the cylinder.

5. Check carrier gas cylinder to see if there is enough gas to last overnight.

6. Return the data system to PETOS> by striking the <SYS> key.

7. Open drive doors and remove discs. Store discs in an appropriate place.

8. Turn off the data system POWER.

9. Turn off printer.

10. If the GC is to be shutdown for an extended period of time, cool down all heated zones, turn off gases and bleed down the gaslines. Then turn off the POWER switch and the STANDBY power to the battery back-up.

2.7 SUITABILITY FOR FIELD USE

Several aspects of the Sigma 2000 GC - 3600 Data station are seen to present problems for field applications. While some of the problems are minor irritations, such as the lack of keyboard input buffer on the data station thus requiring the user to wait for system prompts, other aspects of the software and hardware affect the systems' usefullness for on-site spill response application. Major areas of concern include:

1. The instrumentation was designed to operate under laboratory conditions where power is stable, temperature and humidity are controlled and the hardware is seldom moved. Power stability is crucial for proper operation, as most of the detection systems are based on small variations in current or voltage. Power drops or surges could affect analytical results as well as damaging the instruments. Temperature must be maintained between 15 and 32°C and humidity between 20 and 80 %. Outside the manufacturer's specifications (Appendix E), reliable performance cannot be ensured and many components can be irreparably damaged. The manufacturer is not obligated to honour the warranty if appropriate operating conditions are not observed. Service contracts would be very costly on field instruments, if negotiable. On several occasions during the study, laboratory humidity fell below 20 %, at which time data was lost during acquisition, spurious points were stored in PLOT and REPORT files, and output to the printer caused a myriad of problems.

2. The second area of concern lies with the selection of appropriate detectors. While the PID is significantly more sensitive than the FID for some compounds, it has several inherent problems. The PID requires routine maintenance which is not straightforward. The placement of the graphite disc (Figure 7) is critical. Small particles of graphite 'flaking' off the disc can cause innumerable problems, most of which are difficult to identify. The 'bumps' associated with transporting the GC to the field could render the PID inoperable. Furthermore, the higher sensitivity is not required in most spill situations. The ECD described earlier (2.2.3) is also not

suitable for spill response due to its sensitivity to its environment, its propensity for contamination at high concentrations, and its lengthy stabilization requirements. The FID should cause few problems in the field, however the FID on the Sigma 2000 does not readily ignite (this appears to be a function of its design). The HWD should be considered as an alternative to the PID as it is non-destructive, stabilizes rapidly, detects a wide variety of organics over several ranges in concentration and requires minimal maintenance.

3. The CHROM 2 software, is not menu-accessed, making it necessary to pass through several pages of method information just to change one parameter such as the sample description or data file name. While this does not affect results it is time consuming.

4. The user has no real-time access to parameters, such as endtime, which means unless a long endtime is entered or the compound retention time is known, the user often finds himself in the situation where the peak of interest begins to elute just as the data system terminates the run, losing the data of interest.

5. Parameters such as sampling rate, which severely affect the quality of data, are user definable but are not clearly explained in the user's manuals. Improper selection of sampling rate leads to collection of an excessive number of data points, or worse, collection of an insufficient amount of data for accurate quantitation. Parameters used in Method 'ABC' appear to provide good results for this particular application. If capillary or other types of columns are employed, these parameters must be re-adjusted (see sections 14 of the CHROM 2 instruction manual).

6. Based on the parameters entered, the method indicates the number of runs that can be stored on disc 1, however if there is insufficient disc space the method cannot be overwritten. There appears to be no way of accessing the disc directory to delete files,

short of striking the <SYS> key and entering PETOS, at which time any of the newly entered parameters are lost because the method cannot be overwritten until all the pages are accepted, even though method files are stored on disc 0.

7. If large amounts of data must be stored during acquisition (ie. exceeds the capacity of a peak array), a second array is opened. However integration and reports only include information from the first array. Data from the second array can be accessed by redefining the start time in the method and processing the data with the <PROCESS DATA> key. This situation is not unusual when the multiplex mode is used, especially with capillary columns (ie. fast sampling rate). Again this does not affect data quality but is time consuming.

8. The CHROM 2 software offers very limited control of the integration function. Initial integration is left to the discretion of the software. If the user is not satisfied, base points can be forced using the <INDEPENDENT PEAKS> key. The user is prompted to enter the number of the peak after which the base point should be forced, but is not allowed to define a time at which to force a base point. The <INDEPENDENT PEAKS> key must be used in conjunction with the <PROCESS DATA> function which means data often has to be reintegrated several times before proper integration of one peak is achieved; a time consuming process. The software will allow definition of a start time and end time but the end time is ignored and the end-of-file time is used. The only way of knowing if proper integration has been achieved is by viewing the plot file, which is accessible only when output to the printer. At this time a plot is also displayed on the VDU. Much time could be saved if the plots were displayed on the VDU and the user given the option to output to the printer when satisfied with the integration of all the peaks.

9. If the data system attempts to output to a printer which has not been turned on, the data system responds "NO DSR" and returns the user to PETOS. This error message gives the user no clue that the problem lies with the printer unless the Error Message List is

consulted - Appendix A of the Chromatographics 2 Instruction Manual. If the file from which the output was attempted was a report file, all data must be reprocessed from raw data, assuming it was stored previously. The user is not given the option of turning on the printer and striking a key to continue the output. Other error messages provided by the system are equally mysterious and can only be interpreted using Appendix A of the instruction manual, which is often equally vague.

10. While time allowed for only minimal testing of the data base software, it is apparent that extensive error trapping capabilities must be incorporated to accomodate situations which the 3600 data station cannot handle. Further testing of the software is necessary before it can be used for spill response applications.

Many of the idiosyncracies associated with this data system make it difficult to adapt to field situations where the operator does not fully understand the system and its limitations. Problems such as those with integration may be very subtle and easily overlooked by an untrained eye but nevertheless significantly affect the quality of data produced.

Other than the basic problem of environment control, most of the limititations appear to be software related. While most of the areas of concern do not affect data quality they significantly increase analysis time; an important factor in spill situations. Changes in the software may be possible however the software is written in machine code making such a task very time consuming, even if it can be accessed.

Perkin-Elmer has recently introduced a new chromatography package for the 36000 Data Station, which may not suffer from the same idiosyncracies since it is based on a more powerful microprocessor. However, the software will likely be designed for use by trained personnel and as such may also require modifications if it is to be operated by non-trained personnel.

3.0 INSTRUMENT COMPLIANCE WITH LEVEL 3 ANALYTICAL CONCEPT

The modification of laboratory instrumentation to meet the objectives of the Level 3 concept is not an easy task. All the instrumentation selected was designed to operate under laboratory conditions, where the environment is carefully controlled, reliable power is available and the instruments are seldom, if ever, moved once installed. To take such instrumentation to the field in a mobile laboratory is possible (as witnessed by work done by MOE and EPA), however vehicle suspension must be modified extensively, reliable power sources installed and the vehicles must be climate controlled. Even under these conditions, teams of highly skilled technical people must be employed to ensure that problems can be quickly and accurately identified and solved as they occur. Without such capability, reliable results can not be obtained at the spill site within a useful time period. However, this scenario would be classified as Level 4 under EETD's present scheme.

The Level 3 concept involves the transportation of micro-processor controlled analytical instrumentation to a spill site, or a nearby location, in the back of a small van. Once on-site, the instrumentation is to be set-up and samples analyzed. The instrumentation and software are to be modified such that personnel without extensive training can produce reliable, quantitative results.

However, it is doubtful if laboratory designed instruments will routinely function properly under field conditions and that problems can be adequately diagnosed and eliminated, within a useful time period, without the presence of highly-trained personnel. Furthermore, major difficulties will be encountered in modifying a small van to include adequate suspension, power, climate control and still have sufficient room for the instrumentation.

One alternative to this problem would be to reconsider the definition of the levels and use this instrumentation with the Level 4 concept. To cover the 'gap' created by such a move, some consideration should be given to MTI's Michromonitor Universal Gas Analyzer, or equivalent, which was initially designed for space research and now has been adapted to many other applications. This instrument is a small, high-speed, high-resolution gas

chromatograph which has been designed to survive field conditions. At present, the instrument can identify and quantitate up to 100 different substances from low ppm concentrations to 100% levels. The extent of the analytical capability is defined by the number and type of GC modules purchased. To date, 31 of approximately 55 possible volatile substances, on the EETD priority hazardous substances (Appendix B) are addressed by this system and MTI is constantly upgrading the instruments capability. The instrument is easily operable and does not require that the user have a comprehensive knowledge of the system providing the instrument is operating properly. Only a few keys must be pressed to select the compound(s) of interest, calibrate, and then analyze the sample. Furthermore, analysis times are in the order of seconds.

One limitation of the system is its inability to analyze liquids and solids. However, since airborne contaminants are of highest priority at spill locations this instrument would provide a significant advance in spill response capabilities. While the instrument is new on the market and as such may not be problem-free, the manufacturer appears to be very willing to work with the customer to eliminate problems as quickly as possible, and adjust instrument capability to specific needs of the customer.

Also, the portability of the instrument would allow the purchase of a smaller number of instruments, while maintaining the same level of service to all parts of the country.

APPENDIX A

EVALUATION OF TRS-80 BASED SPECTROSCOPY SYSTEM

Report prepared by Underdown Chemometrics Ltd.,
Nepean, Ontario.

EVALUATION OF TRS-80 BASED SPECTROSCOPY SYSTEM

SUMMARY

The system was developed under contract by Concordia University as part of the Level III on-site spill response program. Its purpose is to allow personnel without an analytical chemical background to use UV and IR spectroscopy to investigate the nature and extent of chemical spills at their site of origin. The equipment should be suitable for transport and use in a van or trailer. It is implicit that such a system should be highly reliable, accurate, and make use of the best hardware and software available within a reasonable price. The system fails to meet any of these criteria. The reasons for this are discussed in the next two sections: Hardware and Software. Detailed description of each part of the system is discussed in the final section.

HARDWARE

The TRS-80 computer is a low priced business/hobbiest oriented 8 bit microcomputer. Since its introduction in the 70's, many more powerful machines have entered the market at only slightly higher cost. It is now possible to purchase a 16 bit computer with main memory and mass storage capacity, processing speed, graphics capability, and interfacing features far superior to the TRS-80 for under $5,000.

The "DAC-2" interface was obviously developed for purposes outside of the present contract. It has many Input/Output ports which are irrelevant to the present application. In spite of the fact that both spectrometers are equipped with standard interfaces for communication with digital computers, analog signals from the spectrometers, meant to drive external hardcopy devices, are converted to digital form. This is unnecessarily complicated and may introduce noise into the signal. While this is not the most serious flaw and does not make the system unsuitable, it is a fundamental design error nevertheless.

The Perkin-Elmer Model 683 infrared spectrometer and Model 552 A UV/Visible spectrometer are modern instruments of suitable quality for the present application. They are internally controlled by microprocessors and can communicate with any computer possessing an RS-232 serial interface for data acquisition purposes. Because the field of microcomputer controlled instrumentation is progressing rapidly, increasingly sophisticated built-in features are appearing on new models each year. Often these features can be added to existing instrumentation by upgrading the computer system to which an interface has been made.

The present system does not control the instrumentation. It only acquires data passively. Computer control of the instrumentation is not necessary in the present application but the computer should be able to function without operator intervention once an analysis is started. This is not possible with the present system in its current state of development. It is necessary to press buttons on both instrument and computer simultaneously. This is an error-prone procedure which could be eliminated by having the computer monitor certain events in the spectrometer such as grating changes.

SOFTWARE

Extensive testing has determined that almost all functions of the system are performed exceedingly slow. It is difficult to know how much of this poor response is due to poor programming since only the object code versions have been supplied for all but one of the programs. This was an unnecessary limitation since TRS-80 programs are normally written in BASIC and then compiled to object code. Since the software was developed specifically for Environment Canada, BASIC program listings should have been supplied.

The system performs most of its specified functions to a limited extent. Data can be acquired from the spectrometers, stored in a "library" file and some comparisons can be made. None of these functions are performed well enough to be useful in a practical working situation. Other specified functions, for example the PRINT function and certain storage operations, could not be performed no matter what was tried.

The programs are not user-friendly. In many cases it requires educated guesses plus trial-and-error to use the programs properly. In some cases, the user has to enter the same data more than once or otherwise perform unnecessary steps to accomplish his or her goals.

RECOMMENDATIONS

Another microcomputer should be found to replace the TRS-80. One possibility which has been discussed by Environment Canada and Farrington, Lockwood Company Limited is using the Perkin-Elmer Model 3600 data station. This computer, originally purchased to control a gas chromatograph, is far superior to the TRS-80. It is based on the Motorola 6800, the most powerful of the 8 bit microprocessors, has good graphics capability, and is supported by Perkin-Elmer, the manufacturer of the spectrometers. The pace of microcomputer development in the last few years has been so rapid, however, that even better computers are now available at a low cost. The fact that spectroscopy software is already available for the Model 3600 weighs heavily in its favour.

The programs developed by Concordia University to build and use libraries for UV/Visible and Infrared spectroscopy would still be inadequate if transferred to a better microcomputer. If BASIC listings of them could be obtained, these might prove useful as a starting point in writing new programs. Before new programs are written, the following steps should be taken:

1) Obtain detailed information from Perkin-Elmer on the capabilities of their UV/Visible and IR spectrooscopy software for the Model 3600 data station.

2) A brief literature review to determine what relevant programs, if any, are in the public domain and could be adapted.

3) Some consultation between Environment Canada and the contractors to determine what type of spectroscopy library system should be developed. (With consideration to the findings of 1) and 2).)

DETAILED DESCRIPTION OF PROGRAMS

The spectroscopy system supplied to the contractor included the following:

1) Perkin-Elmer Model 552A UV/Visible spectrophotometer.
2) Perkin-Elmer Model 683 Infrared spectrophotometer.
3) TRS-80 Model III microcomputer with diskette based operating system, BASIC compiler, and documentation.
4) The "DAC-2" interface unit.
5) An RS-232 connector cable.
6) A TRS-80 acoustic coupler/modem.
7) A Radio Shack DC power supply.
8) 5 diskettes, supplied by Concordia University, pertaining to the spectroscopy system.
9) Three pieces of documentation on the system.

The operation of the spectroscopy system begins by powering up the computer with the "system diskette" in disk drive 0. The user is presented with the following menu:

1) ANALYST
2) DATAAQUI
3) DATABASE
4) PRINT
5) TERMINAL
6) DATAPROC (Spectroscopy and analysis system)
7) BACKUP

This differs from what is described in the documentation in that there it is stated that DATAAQUI is accessed by first choosing "spectroscopy and analysis system".

The DATAPROC program was the first one investigated. It involves comparison of known spectra (library spectra) with user recorded spectra, both on diskette.

To use this program, a diskette containing the spectra should be in disk drive 1 although this is not stated by the program or in the documentation. To experienced microcomputer users this may seem trivial but such instructions are absolutely necessary in "self-contained" systems. This type of omission occurs frequently in the present system.
The user is first prompted for the number of spectra to be accessed. Having entered a number, the user is presented with the following line:

"T = TIME, M = MICRONS, MM = MILLIMICRONS, 1/CM OR CM-1 = 1/CENTIMETERS"

?

By trial and error, it was found that the M,MM,and CM-1 responses tell the program what x-axis units to use when displaying the spectra. The significance of T = TIME is not known. It is not clear why the x-axis scale information is needed at this point since, as will be shown later, it was supposed to be stored along with the spectra. By answering the prompts that follow, one can make the program display stored spectra. An excessive number of prompts have to be used. For example, to display 2 IR spectra one must type in "IR" three times . Entry of the 8 digit spectra identification codes requires pressing the RETURN key once after every digit, ie. 16 times to access two spectra. The spectra are displayed using "GRAPH" or "POINT-TO-POINT" modes. It is difficult to discern any difference between the two modes visually. The "GRAPH" mode toook 10 seconds to display a spectra while the "POINT-TO-POINT" mode required 20 seconds. TRS-80 graphics capability is poor. The spectra are displayed within a 36 by 120 array of rectangles which are either black or white. This results in a frequency resolution of 15 cm-1 compared with an experimental resolution of 2-5 cm-1. The absorbance resolution is about 0.027 absorbance units compared with an experimental resolution of 0.001 units. Furthermore, the white rectangles make the spectra look unlike those represented anywhere else.

Before displaying the spectra, the user is given the choice of displaying U(naltered) or M(assaged) versions. If one chooses "M", one is required to enter an A/T factor and an x-scale shift factor. No documentation is provided as to what these options mean but the "massaging" seems to produce a weighted

average since only one curve is displayed when more than one are accessed. The A/T factor was found to multiply the set of absorbance/transmittance values before displaying them butwithout changing the x-axis label.

The user is also given a P(eaks) option. If this option is chosen the user is prompted, without explanation, with the following line:

"CUT-OFF MINIMUM RATIO A/B OR B/A ?"
"CUT-OFF MINIMUM SUM FOR A+B ?"

The program calculated and displays A+B, A/B, and B/A values at various wavelengths for which these values are above the previously entered minima. The documentation stated that this is to allow the user to choose which peaks are best for analysing a two component mixture.

DATAAQUI

This program is to be used for acquiring data from the spectrophotometers. No information was supplied on how to connect the interface between these instruments and the computer. The "DAC-2" interface unit has 8 analog inputs, 4 digital inputs, 4 digital outputs, and an RS-232 interface. This interface must go to the computer since this is the only type of interface on the computer in its present configuration. Consequently, the spectrometer signal must enter the DAC-2 via one of the 8 analog inputs. On the DAC-2 panel, these inputs are labelled: 0-1 V but the written documentation states that a variable operational amplifier should be used tto adjust the input signal between 2 and 5 volts. By using a variable power supply, it was found that an analog signal between 0-1 volts caused a digital output between 3 and 1000. Immediately after starting the DATAAQUI program the user is prompted with: "CHA # ?" This corresponds to the analog input on the DAC 2 with the proviso that the computer numbers the channels 1-8, whereas the labels on the DAC-2 are marked 0-7. This is not mentioned in the documentation. Once an input channel is specified, an LED above the input lights up. The most likely place to take the IR spectrometer signal is from the "0-1 volt ordinate" terminals on the lower left hand side of the machine. This signal was sent to

the DAC-2 and a spectrum was taken by simultaneously pressing the SCAN button on the spectrometer and any key on the computer keyboard.

The TRS-80 collects points at about 12/second, displaying them on the screen, until another key is pressed. Then the raw data is grouped, and averaged into a 120 point set. The documentation describes this as "integration" to produce a "database" which is poor terminology. The documentation states that the time delays due to grating changes in the IR spectrometer can be accommodated by collecting more than one 120 point set. It would then, in principle, be possible to combine them using the M(assage) feature of the DATAPROC program. In practice this is needlessly complicated since it would not be too difficult to have the computer record and combine two parts of the spectrum automatically.

After data acquisition is terminated and the 120 point set is created, it is displayed on the screen as an unlabelled plot. The user is prompted as to whether the spectrum should be saved. If the response is positive, control is transferred to the database program which asks the user to choose from the following menu:

T to transfer.
L to transfer 120 points to database
C unknown

If the T option is chosen, the program asks the user which database to choose:

IRF/UVF/GCF ?

If IRF is chosen, the program gives the last compound number entered and prompts the user for a number. Given a number, it asks how many compounds to be entered. (This is irrelevant if one has entered DATABASE from DATAAQUI where only one spectra has been acquired.) It then saves the data on drive 1 and goes "dead in the water". ie. no prompts are given and the computer is unresponsive to everything but re-booting. It may be that the T option was originally used for transferring data to another computer. If the L option is chosen, the user is asked for a compound key number with "(999,0,0,0,0,0,0,0)"

as part of the prompt. The program then displays the blank DATABASE format (see page 7 of Concordia documentation) with the cursor on a menu line with the following choices:

P(oints) A(cquisition) D(isplay) E(rase) S(ave) Q(uit) ?

In order to enter the acquired points into the database, one must choose A(cquisition) from the menu. This is an unnecessary step since the user has already chosen to save the points in a previous step. The program requires about 20 seconds to transfer the points as seen by the "-1" 's being replaced with the acquired values. Again, it is not clear why the program does not do this after the user has chosen to save the points and then display the results. Details of using the DATABASE program are discussed below.

After using the DATABASE program to store acquired data, one would often want to re-run DATAAQUI to acquire another data set. Since terminating DATABASE does not return control back to DATAAQUI even if entry into DATABASE was from that program.

DATABASE

The written documentation discusses this program under the heading: DATABASE FORMAT, ie. as an extension of the DATAAQUI program. It describes using the EDIT mode to enter data manually whereas one actually runs the DATABASE program and chooses P(oints) from the top menu line to do this.

The initial stages of DATABASE have already been described above. Pressing P(oints) from the menu linne allows the user to enter spectral data manually starting from a chosen point. Each datum was prompted for with the message: "DATA FOR POINT n (9999)" When the 120th point was entered, the program was automatically terminated and the entered data was lost. No mention of how to avoid this problem is made in the written documentation. It was found that entering "9999" on the 120th point allowed continuation of the program. To insure proper data entry, the written documentation should explain exactly what to do, and the screen prompts should be more explicit. It is still not

clear if it is possible to enter a full 120 point set. The documentation states that several equal data points can be entered by typing: the value followed by "-(the # of entries to be made)". This procedure was ignored by the program which would only accept one datum each time the RETURN key was pressed.

The documentation on pp.6-7 is confusing since no distinction is made between data which must be entered and that which is optional. For example, when boiling-point is compared to x-axis increment, the user should be prompted sequentially for the necessary data, then given the option of entering optional data. It is not properly stated that the procedure for entering or changing data associated with equal signs is to type, for example: UN = 4.5 <RETURN> . Error diagnostics are poor. For example, on S(aving) a spectrum for which the y-axis units were not specified, the following message is displayed on the screen:

" only T or A units can be used for y-axis not,"

The program refused to save some settings (SP=600, IN=28) even though these data were initially accepted by the program and displayed on the DATABASE sheet (p.7 of documentation) in the proper places. Choosing the D(isplay) option appears to do nothing except print some of the data over itself. A more useful option would be to display the spectrum corresponding to the current data. Some of the data formats shown on the DATABASE sccreen were contradictory to what was actually accepted by the program.

PRINT

This program displays the following message on the screen:

"Type the following instructions:

```
LOAD "X"  X = name of file to be found.
SAVE "FILE",A
RUN "PRINT"
```

READY

The program is asking the user to convert the file he wants printed to an ASCII file named "FILE" which it then is supposed to print. This is poor programming since it is trivial to do the above operations totally under program control. The only prompt the user need answer is: "Name of file to be printed ?" In any event, the program does not work. This is not a hardware problem since files from the same diskette were copied to the printer using the DUAL and LIST commands in BASIC.

ANALYST

This program does simple algebraic calculations concerning Beer's Law. etc. It prompts the user for input data and outputs the answer. It works properly.

TERMINAL

This program was not tested since its original purpose was to access the Concordia University mainframe computer and this operation has been removed from consideration by Environment Canada.

SUPPLIED DISKETTES

Several of the supplied diskettes had confusing or wrong labels. One diskette labelled "System Diskette" was definitely not a system diskette. Some diskettes labelled IRBASIC and IRPAT contained the library of spectra previously mentioned. These spectra could be accessed by programs previously discussed. Much of the written documentation discusses programs for compound identification under IRBASIC & IRPAT headings. Apparently these progrrams run on the Concordia University mainframe computer and there was some confusion about whether they had been transferred to the TRS-80. There was no apparent way to enter these programs from the main menu on the system disk and a

careful search of the files on all the supplied diskettes did not locate any such programs.

APPENDIX B

PRIORITY HAZARDOUS SUBSTANCES LIST

Proceedings of the Technical Seminar
on Chemical Spills, Toronto, 1983.
Environment Canada publication

LIST OF PRIORITY HAZARDOUS MATERIALS FOR THE
ENVIRONMENTAL EMERGENCY BRANCH
The 50 Highest Priority Chemicals
(In Alphabetical Order)

Acetic Acid
Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Butyraldehydes
Calcium Chloride
Calcium Oxide/Hydroxide
Carbon Dioxide
Chlorine
Cyclohexane
Ethylbenzene
Ethylene
Ethylene Dichloride (1,2-Dichloroethane)
Ethylene Glycol
Ethylene Oxide
Ferric Chloride
Formaldehyde
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Sulfide
Mercury
Methanol
Morpholine
Naphtha
Natural Gas
Nitric Acid
Phenol
Phosphoric Acid
Phosphorous
Potash (Potassium Chloride)
Propylene
Propylene Oxide
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Hypochlorite
Sodium Sulfate
Styrene (Monomer)
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Sulfur
Tetraethyl Lead
Toluene
Urea
Vinyl Chloride
Xylenes
Zinc Sulfate
2-Ethylhexanol

THE SECOND GROUP OF PRIORITY CHEMICALS
(100 substances or groups)

Acetone
Acetylene
Acrylonitrile
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Aminocarb Pesticide (Matacil)
Ammonium Chloride
Ammonium Sulfate
Arsine
Barium Sulfate
Benzoic Acid
Borax
Boric Acid
Butanols
Butylene
Calcium Carbide
Calcium Carbonate
Calcium Hypochlorite
Calcium Phosphate
Caprolactam
Carbaryl
Carbofuran Pesticides
Carbon Disulfide
Carbon Tetrachloride
Chlordane
Chloroform
Copper Sulfate
Cresols
Dicamba
Dichlorobenzene
Dimethyl Ether
Dimethyl Terephthalate
Dinoseb
Diphenylmethane-4,4'-Diisocyanate
Ethanolamine
Ethanol
Ethylene Dibromide
Fenitrothion
Fluorochloromethanes
Formic Acid
Hydrazine
Hydrogen Peroxide
Hydrogen
Ispropanol
Ispropylbenzene
Latex
Lead Chromate
Lead Oxides
Magnesium Hydroxide
Malathion
Maleic Anhydride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate
Methylamines
Methylene Chloride
MCPA
n-Hexane
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Pentaerythritol
Perchloroethylene
Phthalic Anhydride
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Hydrosulfite (Dithionite)
Sodium Phosphates
Sodium Silicates
Sodium Sulfite
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Titanium Dioxide
Triallate Pesticides
Trichlorfon Pesticides
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Vinyl Acetate
Yellow Cake
Zinc Chloride
Zinc Oxide
1,1,1-Trichloroethane
1,3-Butadiene
2,4-D (2,4-Dichlorophenoxyacetic Acid)
2,4-Toluene Diisocyanate

APPENDIX C

CHROMATOGRAPHY LIBRARY SYSTEM DOCUMENTATION

Report prepared by Underdown Chemometrics Ltd.,
Nepean, Ontario.

CHROMATOGRAPHY LIBRARY SYSTEM DOCUMENTATION

SECTION 1. - Introduction

The Chromatography Library System was developed in part by Underdown Chemometrics Limited for Farrington, Lockwood Company Limited as part of contract KE145-3-0282 for Environment Canada. The system lets one build a library containing information on up to two hundred known compounds. Results for each peak in a multicomponent mixture can be compared with each entry in the library using the following criteria:

1) FID retention times (relative to benzene standard)
2) PID retention times (relative to benzene standard)
3) Peak area ratio (PID/FID)

A list of the five closest library compounds using these criteria is produced for each peak in the mixture. Quantitation is performed using FID and PID response factors for each of the known compounds. Variation in absolute detector response over time is corrected for by calculating the peak areas of both library compounds and sample components relative to a benzene standard. Provision is made for building the library with average data from several runs . Compounds which produce a useful response on one detector only, can be entered into and compared with the library. The system keeps track of which comparisons and calculations are possible .

The programs which comprise the library system are written in Microsoft BASIC and run on the Model 3600 data station. They are documented in increasing detail in the following three sections:

Section 2.- General Description
Section 3.- Instructions on program use
Section 4.- Technical Description

Section 2. explains what each program does and how the programs are inter-related. Section 3. provides instructions which should be read before

using the system and kept on hand during a session. Section 4. contains the BASIC listings plus an explanation of each variable name used in the programs. This section is meant to facilitate the modification of the system's programs at a later date if needed.

SECTION 2. - General Description

PROGRAM BUILD:

This program is run when data on known compounds is to be entered into the library. Peak areas and retention times for both the known compound and a benzene standard are entered from the keyboard. The program divides the retention times of the known compounds by the corresponding values for the benzene standard. These relative retention times, for both FID and PID detectors, are written into the library file. Similarly the sample peak areas are divided by the corresponding benzene values to produce relative peak areas. These relative peak areas are further divided by the sample volume as input from the keyboard. The resulting value, relative peak area per unit volume of sample, is a response factor which can be used for quantitation. Response factors for both FID and PID detectors are written into the library file.

The library file which is created by BUILD is called MLIB1. and is a random access file (see "BASIC PROGRAMMING THE MODEL 3600 DATA STATION") in which each line has the following information:

Compound Name	Lib. #	Relative PID Retention Time	Relative FID Retention Time	Relative PID/FID Peak Area	PID Response Factor	FID Response Factor

PROGRAMS COMP1 and COMP2

These programs are used to compare data on multicomponent samples with the data on known compounds in the library. Version COMP1 allows one to input sample data by reading report files which have been created by the CHROM 2 chromatography program. Version COMP2 allows one to input sample data from files built from the program: RPORT. This latter method can be used if the CHROM 2 report files for a particular experiment have been printed but were either not saved on diskette or were produced by a format other than the "Area-Height Percent" format.(See CHROM 2 manual: p. 4.8) In both versions the benzene standard data is input from the keyboard.

The program calculates the values of the variables used for identification for each component and the user selects which one he wants to use. The library is then searched using that criterion and a list of the five closest compounds is displayed along with the possible amount present using library response factors. The user is then allowed to choose another criterion for identification. It is up to the user to decide which library compound corresponds to each peak. This is best accomplished using the lists produced by each identification criterion plus knowledge about the origin of the sample.

In order for PID/FID peak area ratios to be meaningful in a multicomponent mixture, the program must match up the correct peaks from both detectors. If all components show up on both detectors this is a trivial problem but if there is one or more missing peaks from either detector, problems can arise. The programs check for this in two ways:

i) Equal #'s of peaks in both report files.

ii) Corresponding peaks must fall within a specified time interval relative to each other.

If either of these conditions is not filled, a message will be displayed and PID/FID peak area ratios will be prevented. Identification using retention

times will, of course, still be possible.

In addition to selecting the identification criterion, the user may also work with any subset of component peaks. This allows one to work with only those components of interest to save time. Also PID/FID correspondence conditions discussed above are checked for on the subset of peaks. The correspondence problem will then be eliminated if it involves peaks occuring later than those in the subset of interest.

PROGRAM RPORT

This program allows one to build report files on multicomponent samples by entering the peak areas and retention times from the keyboard. These report files can be read by the program COMP2 in the same way that the CHROM 2 report files are read by COMP1. This procedure can be used when CHROM 2 report files using the Area-Height Percent format are not available on diskette.

PROGRAM RREAD

This program will print out, line by line, any ASCII file on diskette. It prints out the line number of each line including those lines which are blanks. It was originally used to determine the format of the CHROM 2 report files so that they could be input by COMP1. Possible future uses include looking at the CHROM 2 report files created using formats other than Area-Height Percent. This would facilitate modification of COMP2 to read these files.

SECTION 3 - Operating Instructions

GENERAL

First of all, the following files should be copied onto the CHROM 2 back-up diskette:

BUILD.BA
COMP1.BA
COMP2.BA
RPORT.BA
RREAD.BA

Do this using the COPY utility as explained in the Perkin-Elmer manual: "MODEL 3600 DATA STATION", section 5.

All chromatography operations can be carried out with the CHROM 2 backup diskette in drive 0 and a formatted data diskette in drive 1. The CHROM 2 and RPORT programs will write report files onto the diskette in drive 1. Also the BUILD program will create and add to the library file on the diskette in drive 1. This allows for some flexibility since different library files (each called MLIB1.BA) can be created on different diskettes. A specific version of this file can also be copied to other data diskettes. It is up to the user, however, to keep track of these files, keeping in mind that only one file called MLIB1.BA can exist on each diskette. The file MLIB1.BA is a random access file in which each record can be written to and read without modifying any other record in the file. (See BASIC PROGRAMMING THE 3600 DATA STATION, P.8.4)

RUNNING CHROM 2

Complete documentation for this program is provided in the Perkin-Elmer manual: CHROMATOGRAPHICS 2. It is anticipated that the chromatography experiment will be carried out in the Multiplex mode in which data is collected for both detectors simultaneously and written in two separate report files. In this manner, report files of the Area-Height Percent type can be

generated for the following sets of data:

When Running Known Compounds:

Report File	Suggested Name	Save on Diskette?
FID Detector - Benzene	FBxxx	-
FID Detector - Compound	FCxxx	-
PID Detector - Benzene	PBxxx	-
PID Detector - Compound	PCxxx	-

When Running Samples :

Report File	Suggested Name	Save on Diskette?
FID Detector - Benzene	FBxxx	-
FID Detector - Sample	FSxxx	YES
PID Detector - Benzene	PBxxx	-
PID Detector - Sample	PSxxx	YES

Of course, any of the report files can be saved on diskette. The entries in the above table indicate the ones which are needed by other programs. The report files which are not saved on diskette should be output to the printer since they contain data which will input to other programs from the keyboard. When running known compounds, bear in mind that one has the option of running several repetitions for averaging when the COMP1 program is run. It is not necessary to run a standard for each of these repetitions since the data for the relevant benzene run can be entered more than once. There is no provision for averaging sample runs since chromatography experiments take some time and it will be desirable to process results one by one. Thus library searching can be performed on data from a sample run while data from a second sample is being collected using the chromatography interface in the stand alone mode.

RUNNING BUILD

This program requires peak area and retention time data for known compounds and the benzene standard for each detector. See table on preceeding page. Be sure that the CHROM 2 backup diskette is in drive 0 and the formatted data diskette to contain the library file (MLIB1.BA) is in drive 1. One should see the PETOS> prompt on the screen. If not, press the <SYS> key and type: CA <RET>. This cancels the present task and returns control to PETOS>. Now type: BASIC. The system will load BASIC and display the READY: prompt on the screen. Type: LOAD "MFD0:BUILD" <RET> and then type: RUN <RET>.

The program will then prompt for various data. Enter the concentration in units of ng and the peak areas in "counts" as appears in the Report Files. Enter time in seconds or minutes (ie 21.9 min). The program allows one to enter up to 10 repeats of each data set. Type: 0 <RET> after the last data set has been entered. If there is no data of a particular type - for instance, no FID data - Type: 0 <RET> when first prompted for that set of data.

When all the data for a specific compound has been input, the program will do its calculations and write a record into the file MLIB1.BA in drive 1. If the file does not exist, a new one will be created. The program will then end with the prompt: READY: returning to the screen. To enter data for another known compound, type: RUN <RET> again. To go back to PETOS>, press the <SYS> key and then type: CA <RET>> to cancel BASIC.

The BUILD program will also create a file (SLIB.) which is not used at this time but which contains necessary information for statistical calculations and/or error trapping routines.

RUNNING COMP1

Start off with the CHROM 2 backup diskette containing the COMP1.BA file in drive 0 and the data diskette containing the MLIB1.BA file in drive 1. Make sure you have the PETOS> prompt by pressing the <SYS> key, if necessary. Type: CA <RET> to cancel any current task. Then type: BASIC/20 <RET>. BASIC will be

loaded with the extra memory allocation needed to run this program. Now type: RUN <RET>. The program will prompt you for the names of the FID and PID report files containing the results for the unknown sample. It is a good idea to have the printouts of the report files for both detectors and for the sample and the corresponding benzene standard on hand. (four report files in all) There is no need to add the "MFD1:" extension to these file names since the program does this automatically. The program will then prompt you for retention times and peak areas for the benzene standard (both detectors). Read this data from the report file printouts and input it through the keyboard. The program will also prompt the user for the volume of sample injected.

At this point the program will prompt you for the earliest and latest peaks which you want to be processed. If you only wish to look at the third peak, type in: 3 for both these prompts. Shortly after this, the program may inform you if there is a correspondence problem for one of the peaks within the subset you have chosen to be processed. You may still proceed with identification and quantitation for any of these peaks using FID and PID data separately. You may not, however, use PID/FID peak area ratios as an identification criterion. The program will present you with the following menu:

Press and enter:	1	for FID retention times
	2	foor PID retention times
	3	for PID/FID area ratios
	4	to select different peaks for analysis
	5	to end session

Enter your choice and press the <RET> key. After performing the required operation, the program will return to this menu. The following pages show typical program output. The five closest library compounds for each peak in the subset you have chosen to work with will be listed in the first column. The second column lists the difference in the variable used as the searching criterion (relative retention time for menu choices 1 and 2, PID/FID peak area ratio for choice 3) between the library compounds and the components of the sample. Columns 3 and 4 show the amount of library compound present ng/uL or ppm. Note that these amounts are based on the response factors of the library

compounds and are thus hypothetical. Only the amount present for the identified compound is meaningful. No quantitation is done for the PID/FID peak area ratio option (choice 3) since both quantitation methods are covered with choices 1 and 2. Choose option 4 to change the subset of peaks for comparison with the library. Note that if you choose option 3 when the program has already determined that it is not possible, the program will display a message to that effect on the screen and return to the main menu. To perform library comparisons with another sample, choose option 5 to end the session and type: RUN <RET> to start the program again.

RUNNING COMP2

This program is almost identical to COMP1 except that it reads report files created by the RPORT program instead of those created by CHROM 2. Please refer to the preceeding section: RUNNING COMP1 and the following section: RUNNING RPORT.

RUNNING RPORT

This program is to be used when report files using the Area - Height Percent format and created by CHROM 2 have not been saved on diskette but the peak areas and retention times for the components of a sample and the benzene standard have been recorded on paper.

Load and run this program using BASIC in the same manner as the program BUILD. (Refer to the section RUNNING BUILD). The program will prompt you for the name of the file to be created. Choose a name consistent with the naming scheme on p.4 but be careful not to duplicate the name of a previous report file, including one created by CHROM 2. The prefix "MFD1:" will be added to the file name already entered. The program will then prompt you for the information on sample peaks in a straightforward manner. Enter the retention times and peak areas in the units used by CHROM 2: seconds and counts respectively. For each sample, create two report files: one for FID results and one for PID results. Although the report files created by CHROM 2 and RPORT have different formats,

there is no problem with them residing on the same diskette providing two rules are followed:

1) All report files must have unique names.

2) Read CHROM 2 report files with COMP1 and RPORT report files with COMP2.

RUNNING READ

Load and run this program in the standard manner for BASIC programs. (See first few lines of RUNNING BUILD) The program will prompt you for the name of the file to be read. Once again the prefix "MFD1:" is not necessary since the program will add this to the name you type in. Of course, the file you want to read should be in drive 1.

Test Examples

For Peak #1 in chromatogram
Five closest matches with library using FID retention times

Compound	Reten. time diff.	Amount
test 1	0.002	1.004
test 11	0.002	1.004
test 6	0.074	1.985
test 10	0.145	0.817
test 9	0.158	1.051

For Peak # 2 in chromatogram
Five closest matches with library using FID retention times

Compound	Reten. time diff.	Amount
test 7	0.000	1.000
test 8	0.152	0.922
test 3	0.213	0.728
test 2	0.549	0.418
test 9	0.579	0.606

For Peak # 3 in chromatogram
Five closest matches with library using FID retention times

Compound	Reten. time diff.	Amount
test 10	0.040	0.864
test 1	0.107	1.062
test 11	0.107	1.062
test 6	0.179	2.100
test 9	0.263	1.111

For Peak # 1 in chromatogram
Five closest matches with library using PID retention times

Compound	Reten. time diff.	Amount
test 1	0.002	0.996
test 11	0.002	0.996
test 5	0.099	1.100
test 10	0.143	0.423
test 9	0.154	0.388

For Peak # 2 in chromatogram
Five closest matches with library using PID retention times

Compound	Reten. time diff.	Amount
test 7	0.000	1.100
test 4	0.121	0.539
test 8	0.148	0.360
test 2	0.535	0.832
test 9	0.564	0.565

For Peak # 3 in chromatogram
Five closest matches with library using PID retention times

Compound	Reten. time diff.	Amount
test 5	0.003	2.600
test 10	0.041	1.000
test 1	0.104	2.354
test 11	0.104	2.354
test 9	0.256	0.918

For Peak # 1 in chromatogram
Five closest matches with library using PID/FID peak area ratios

Compound	Peak area ratio Diff.
test 1	0.001
test 11	0.001
test 2	0.029
test 10	0.131
test 7	0.161

For Peak # 2 in chromatogram
Five closest matches with library using PID/FID peak area ratios

Compound	Peak area ratio Diff.
test 7	0.000
test 10	0.030
test 9	0.111
test 2	0.132
test 1	0.160

For Peak # 3 in chromatogram
Five closest matches with library using PID/FID peak area ratios

Compound	Peak area ratio Diff.
test 10	0.000
test 7	0.030
test 2	0.102
test 1	0.130
test 11	0.130

Section 4. - Technical Description

Below are listed the main variables used in programs BUILD, COMP1 and COMP2 along with identifying comments:

TBF - array, FID retention times of benzene standard.
TBP - array, PID retention times of benzene standard.
TCF - array, FID retention times of compound.
TCP - array, PID retention times of compound.
ABF - array, FID peak areas of benzene standard.
ABP - array, PID peak areas of benzene standard.
ACF - array, FID peak areas of compound.
ACP - array, PID peak areas of compound.
RTF - array, relative FID retention times: TCF/TBF.
RTP - array, relative PID retention times: TCP/TBP.
RA - array, ratio of peak areas : ACP/ACF.
KF - array, FID response factor of compound: ACF/(V*ABF).
KP - array, PID response factor of compound: ACP/(V*ABP).

The use of these array variables is somewhat different between programs build and programs COMP1 and COMP2. In BUILD, the elements of the array correspond to different repeats on the same known compound. In the COMP programs, the elements correspond to different components of a single sample.

MRTF - mean values of RTF written to library file by BUILD.
MRTP - mean values of RTP written to library file by BUILD.
MRA - mean values of RA written to library file by BUILD.
MKF - mean values of KF written to library file by BUILD.
MKP - mean values of KP written to library file by BUILD.

SRTF - standard deviation of RTF written to file, SLIB1 by BUILD.
SRTP - " " RTP " "
SRA - " " RA " "
SKF - " " KF " "
SKP - " " KP " "

LRTF - library value of RTF read from MLIB1 by COMP1, COMP2.
LRTP - " " RTP " "
LRA - " " RA " "
LKF - " " KF " "
LKP - " " KP " "

The other variable names used in the programs can be easily understood by studying the program listings.

APPENDIX D

CALIBRATION DATA AND PLOTS

DATABASE 1

Compound	Lib. No.	Amount (ng)	Time min (sec)	PID Area	FID Area
Benzene	1	439.4	21.90(1314)	1832688	178649
Acetone	2	500	7.88(472.8)	775377	78296
Carbon disulfide	3	500	9.27(556.2)	96135	----
Carbon tetrachloride	4	1000	18.19(1091.4)	----	25218
Chloroform	5	1000	15.01(900.6)	----	34522
Cyclohexane	6	1000	18.16(1089.6)	427653	292070
Dibromoethane	7	2000	20.21(1212.6)	----	92943
Ethylene dichloride	8	1000	15.99(959.4)	----	90298
n-Hexane	9	1000	23.59(1415.4)	13362	282838
Isopropanol	10	1000	9.31(558.6)	25997	135664
Methyl ethyl ketone (MEK)	11	500	15.89(953.4)	851542	92598
Methyl isobutyl ketone (MIBK)	12	500	25.63(1537.8)	784947	189289
Methylene chloride	13	1000	7.24(434.4)	28932	45884
Tetrachloroethylene	14	500	27.94(1676.4)	693154	27132
Toluene	15	500	38.22(2613.2)	1496869	162198

1. Library entries referenced against an average of 12 benzene runs at 439.4 ng: PID area - 1371582, FID area - 146305.

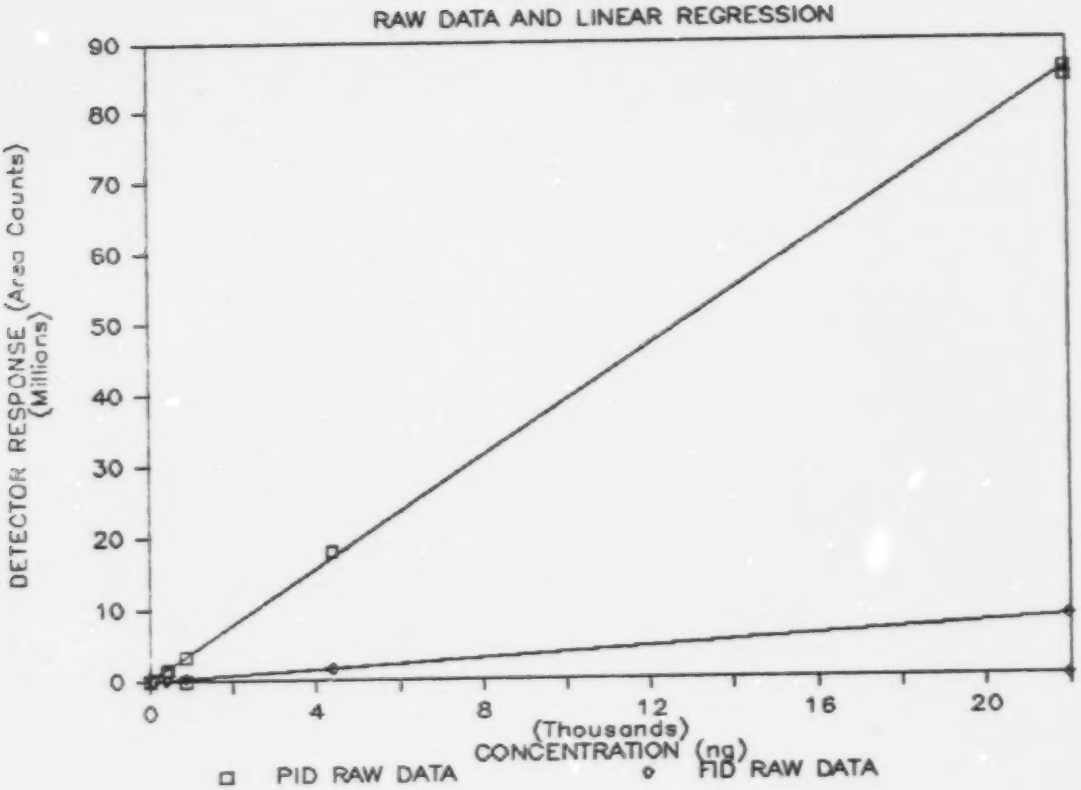
2. Detector areas calculated from results of linear regression analysis using hypothetical concentrations.

Compounds attempted but not used in Database at this time

Dichlorobenzene	- chromatographic difficulties
Ethanol	- data non-linear
Ethyl benzene	- quantitative standard unavailable
Formaldehyde	- quantitative standard unavailable
Isopropyl benzene	- quantitative standard unavailable
Methanol	- data non-linear
Phenol	- chromatographic difficulties
Styrene	- chromatographic difficulties
1,1,1-Trichloroethane	- quantitative standard unavailable
Vinyl acetate	- quantitative standard unavailable
Xylenes	- chromatographic difficulties
Acrylonitrile	- does not chromatograph under these conditions
2-Ethyl hexanol	- does not chromatograph under these conditions

BENZENE

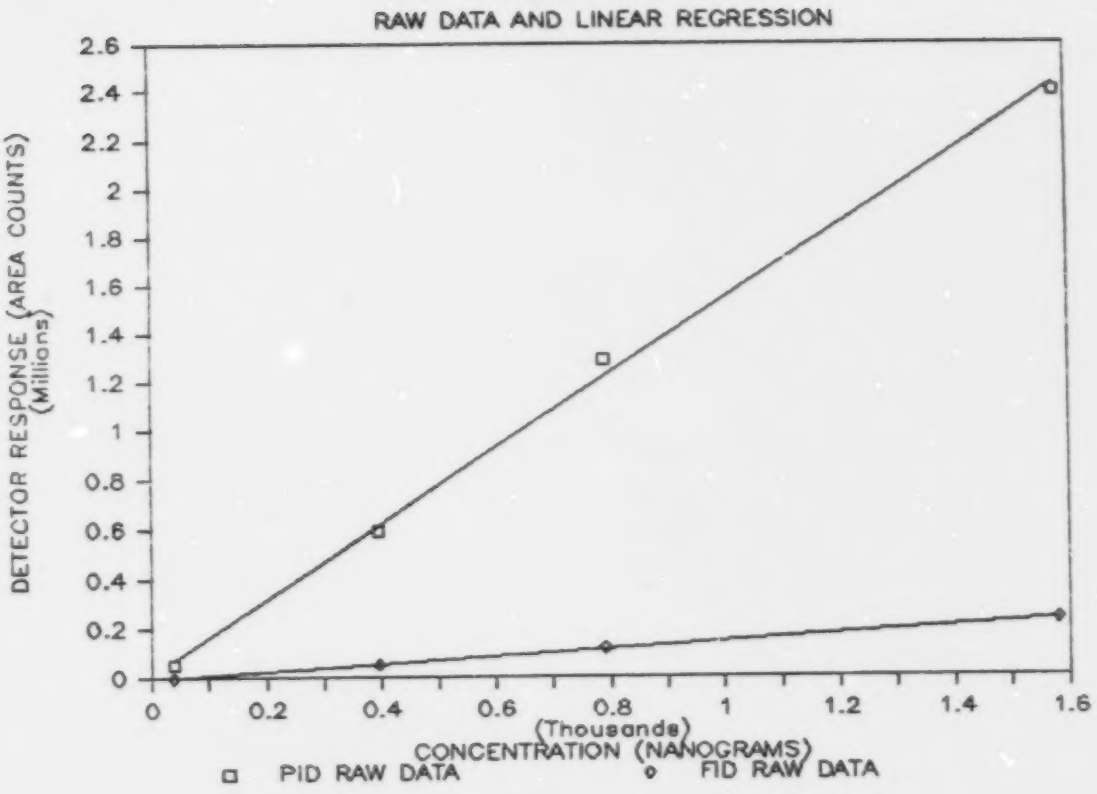
RAW DATA AND LINEAR REGRESSION



INCL. LIN. REGR. (Y/N)	BENZENE STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
NO	0.8787	16470	1428
NO	8.787	50746	4269
YES	87.87	347397	34683
YES	399.40	1454035	147938
YES	439.40	1725721	181941
YES	878.70	3347200	345524
YES	4393.50	16008900	1657222
YES	21967.50	85492700	8320500
NO	878.70	---	330667
NO	21967.50	84212700	---
	SLOPE	3893	378.5
	INTERCEPT	122104	4556
	CORR.COEFF.	0.9999	1.0000

RESPONSE RATIO PID/FID= 10.29

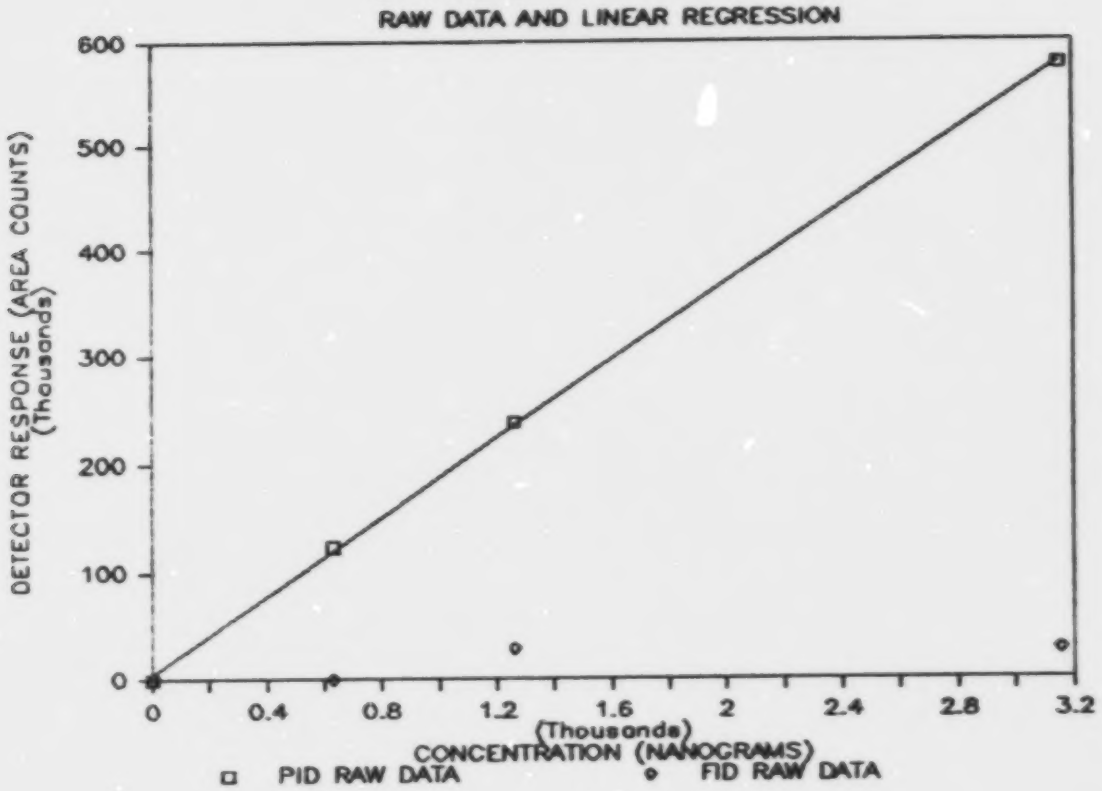
ACETONE



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	39.54	55695	N/D (0)
YES	395.40	591345	52343
YES	790.80	1287600	118561
YES	1581.60	2398558	233739
	SLOPE	1527	152.3
	INTERCEPT	11877	-5704
	CORR.COEFF.	0.9990	0.9996

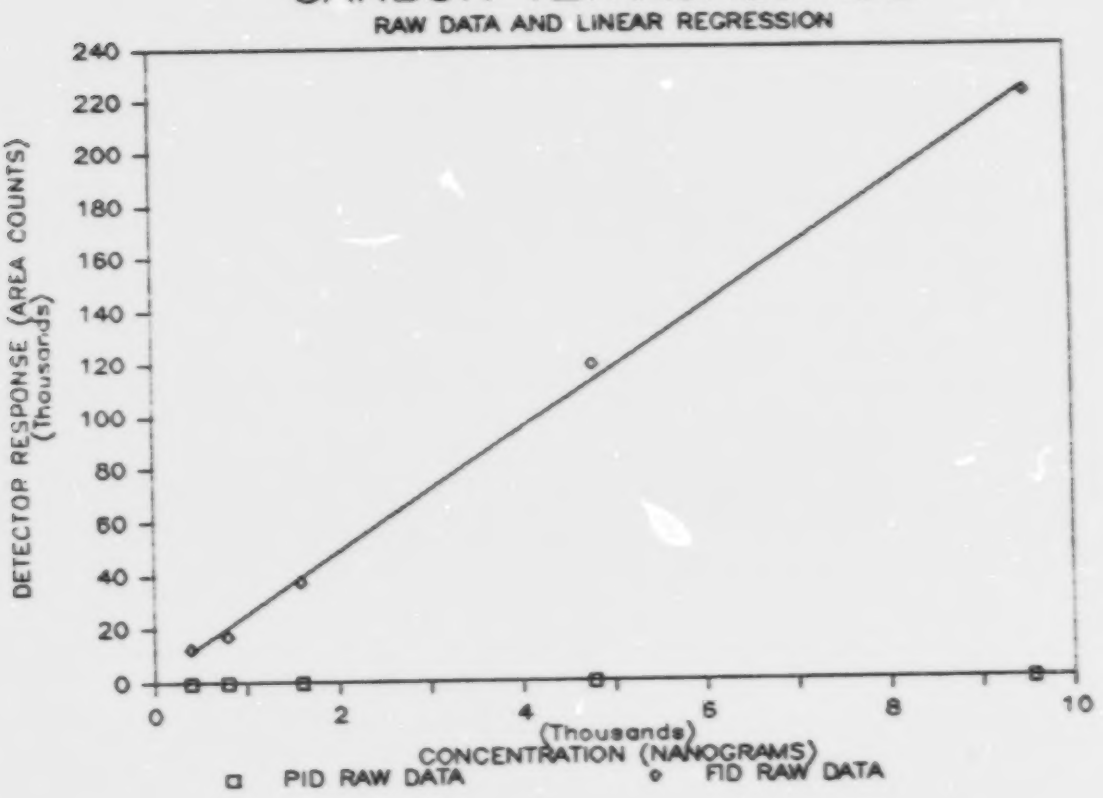
RESPONSE RATIO PID/FID= 10.03

CARBON DISULFIDE



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	0.00	0	0
YES	631.40	123628	0
YES	1262.80	238260	28297
YES	3157.00	576787	27260
	SLOPE	181.8	---
	INTERCEPT	5135	---
	CORR.COEFF.	0.9998	---
RESPONSE RATIO PID/FID=		---	

CARBON TETRACHLORIDE

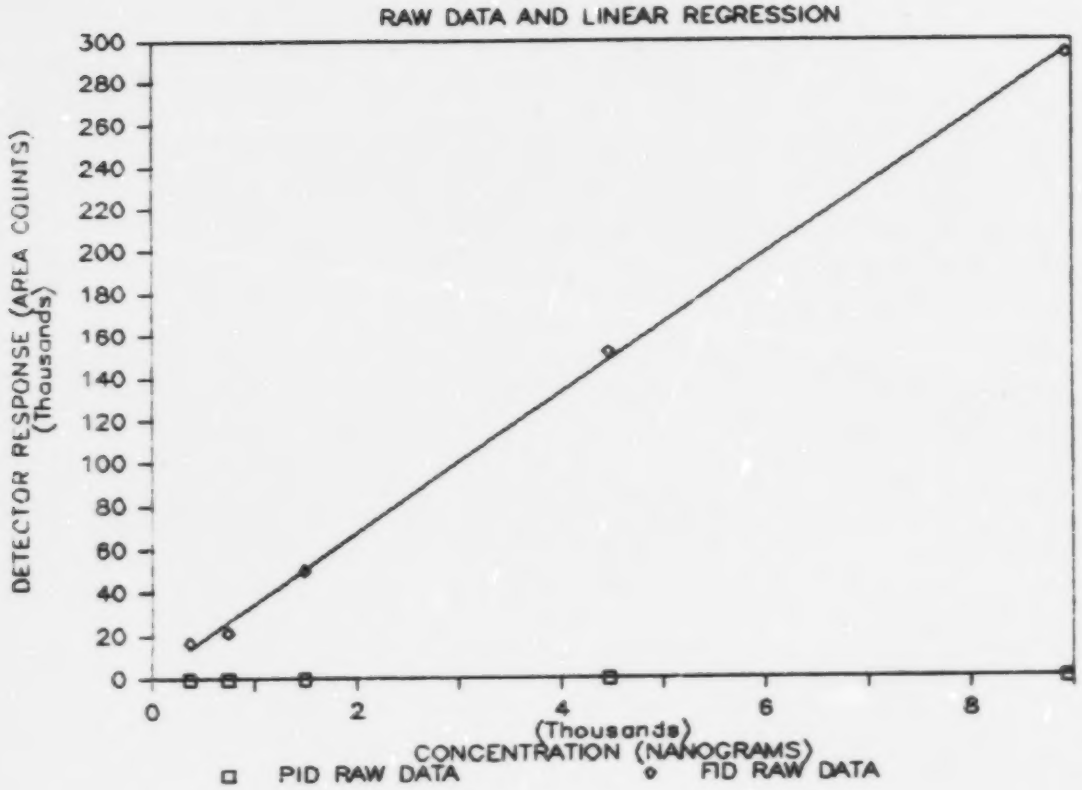


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	9565.20	0	221364
YES	4782.60	0	118875
YES	1594.20	0	37527
YES	797.10	0	17240
YES	398.60	0	12586
	SLOPE	0	23.19
	INTERCEPT	0	2025
	CORR.COEFF.	0.0000	0.9991

RESPONSE RATIO PID/FID= 0.00

CHLOROFORM

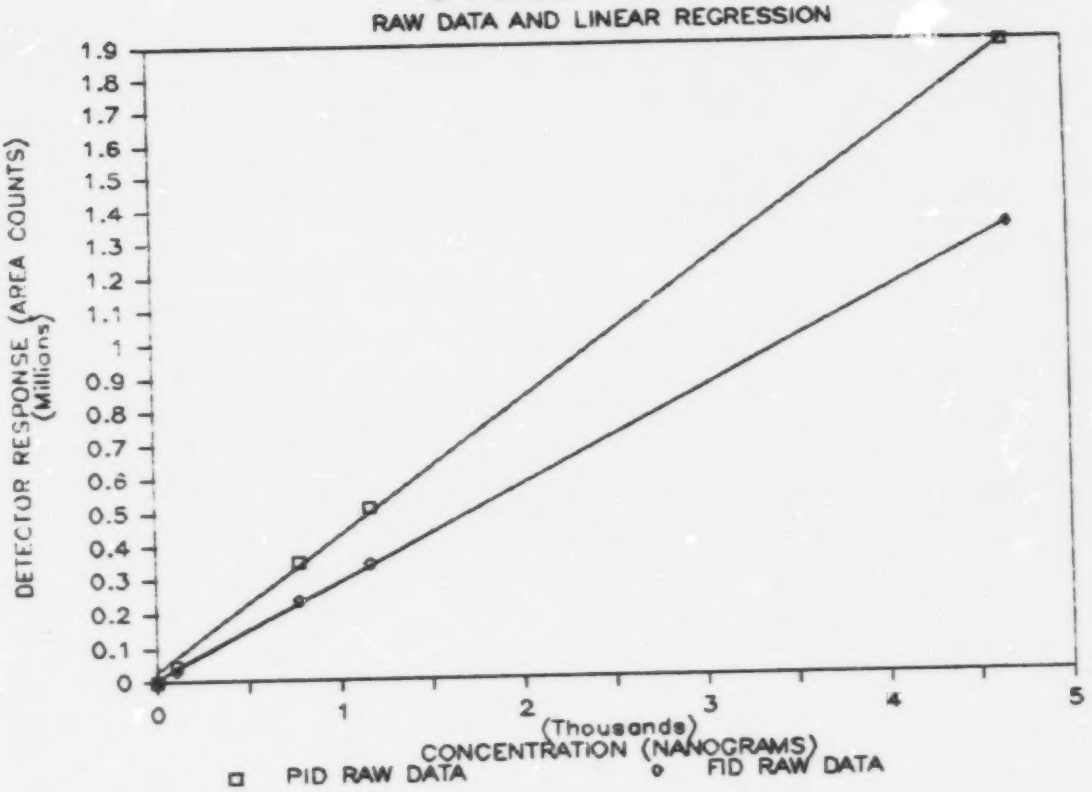
RAW DATA AND LINEAR REGRESSION



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	8949.60	0	293083
YES	4474.80	0	151639
YES	1491.60	0	50165
YES	745.80	0	21502
YES	372.90	0	17078
	SLOPE	0	32.70
	INTERCEPT	0	1821
	CORR.COEFF.	0.0000	0.9996

RESPONSE RATIO PID/FID= 0.00

CYCLOHEXANE

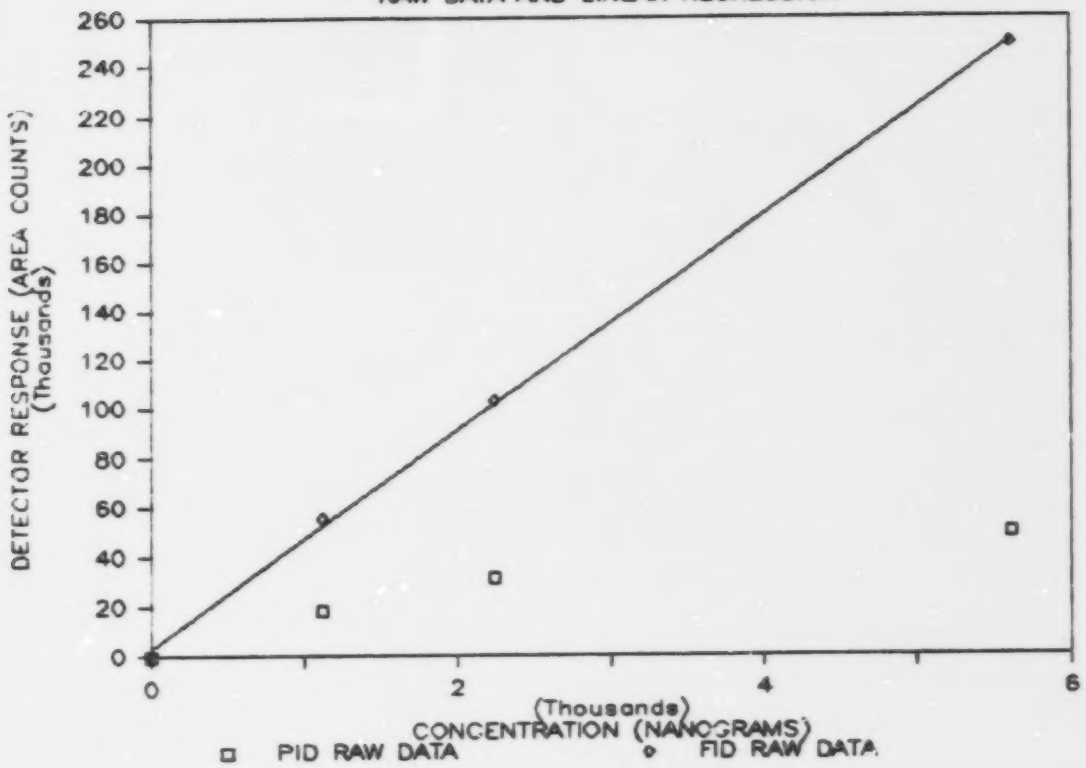


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
NO	0.00	0	0
YES	4674.60	1898864	1331548
YES	1168.65	518478	345358
YES	779.10	352241	236215
YES	186.24	46938	29797
	SLOPE	399.8	283.4
	INTERCEPT	27653	9878
	CORR.COEFF.	0.9998	0.9999

RESPONSE RATIO PID/FID= 1.41

DIBROMOETHANE

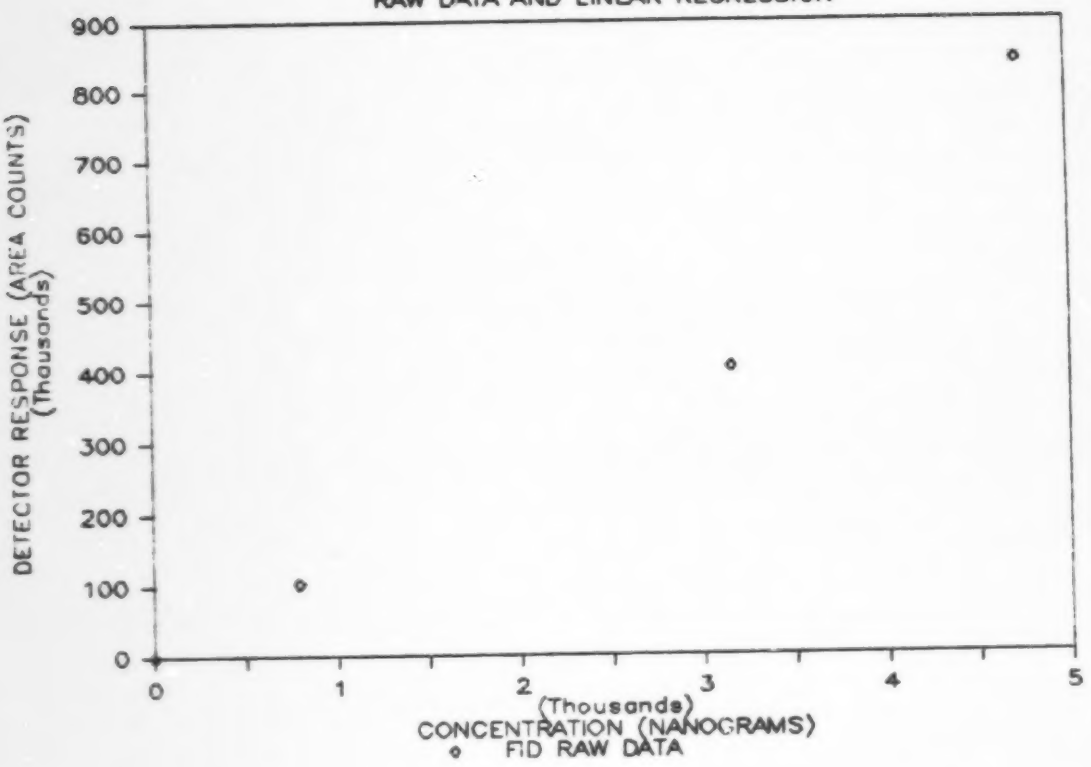
RAW DATA AND LINEAR REGRESSION



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	0.00	0	0
YES	1123.20	18048	55053
YES	2246.40	31062	103042
YES	5616.00	49001	249058
	SLOPE	---	44.01
	INTERCEPT	---	2914
	CORR.COEFF.	---	0.9997
RESPONSE RATIO PID/FID=		---	

ETHANOL

RAW DATA AND LINEAR REGRESSION



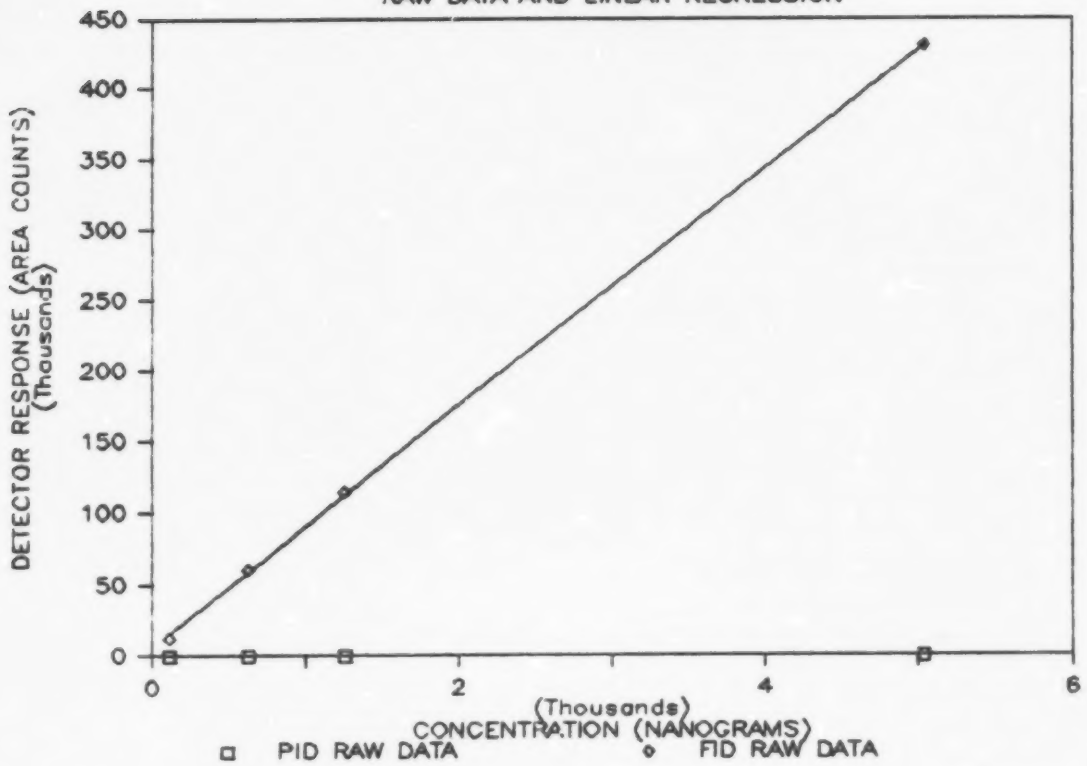
INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	0.00	---	0
YES	789.30	---	103072
YES	3157.20	---	404733
YES	4735.80	---	839117
	SLOPE	---	---
	INTERCEPT	---	---
	CORR.COEFF.	---	---

RESPONSE RATIO PID/FID= ---

NOTE : DATA NOT SUITABLE FOR REGRESSION - CHROMATOGRAPHY PROBLEM.

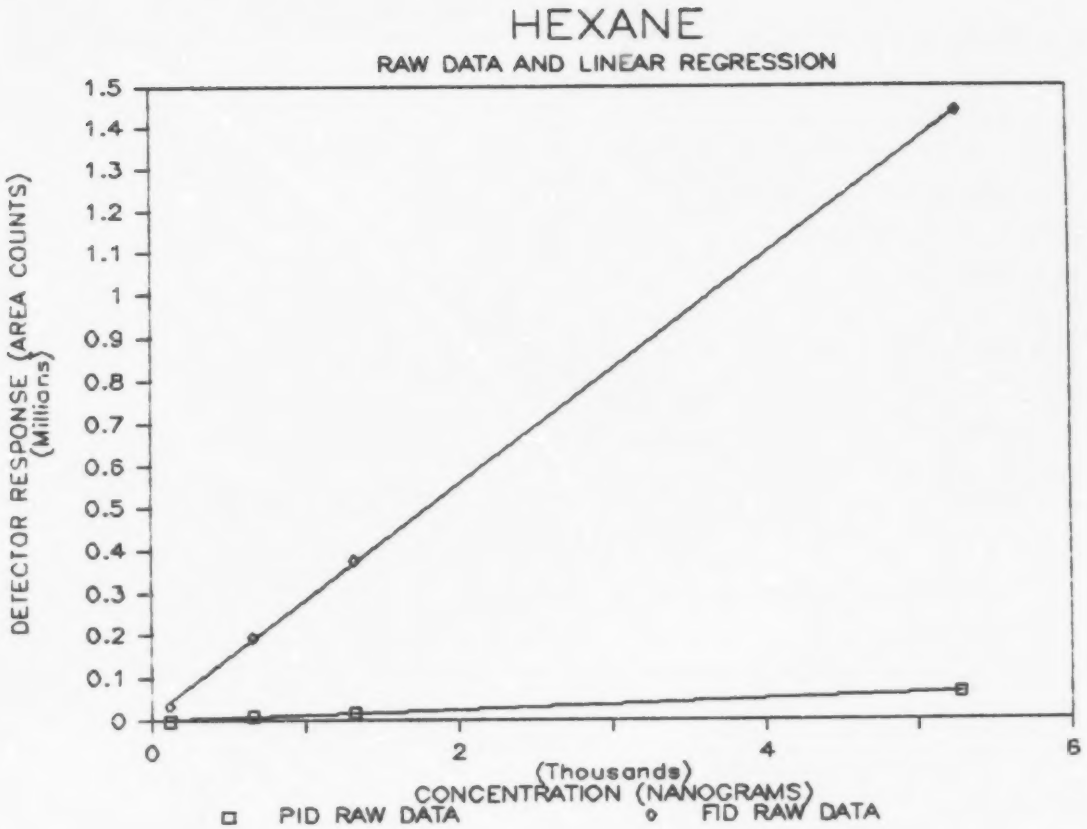
ETHYLENE DICHLORIDE

RAW DATA AND LINEAR REGRESSION



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	5040.00	0	430322
YES	1260.00	0	114254
YES	630.00	0	60904
YES	114.54	0	12452
	SLOPE	0	84.33
	INTERCEPT	0	5970
	CORR.COEFF.	0.0000	0.9999

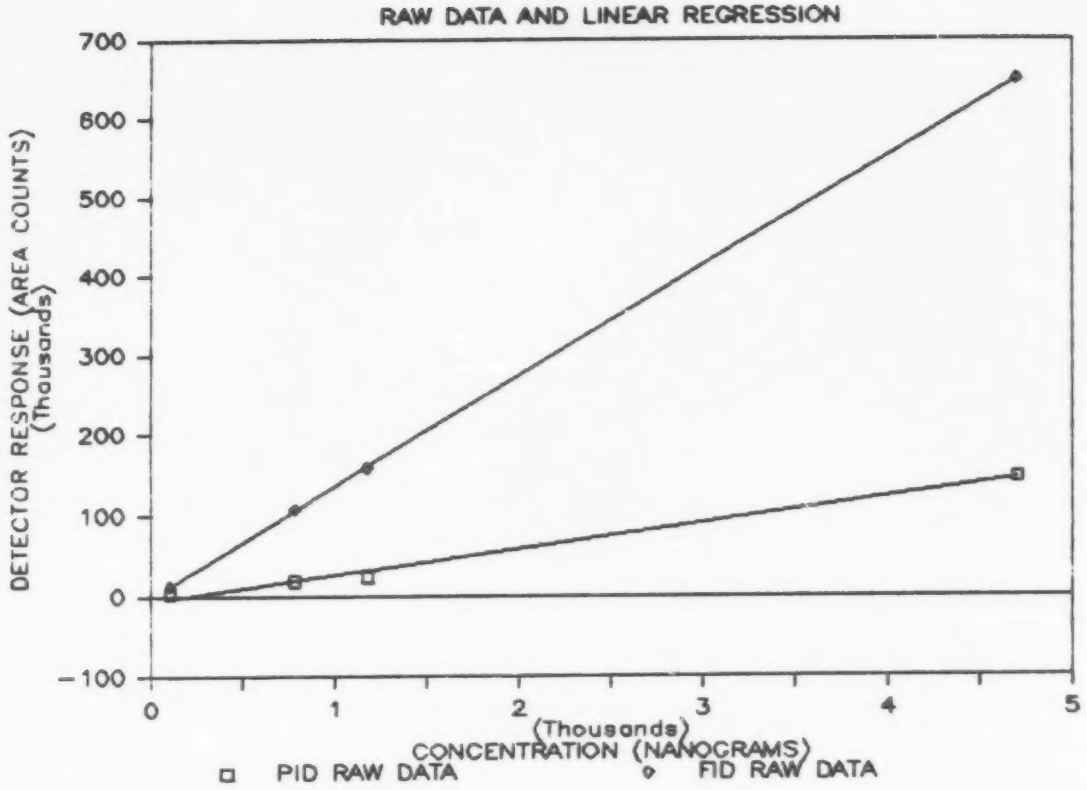
RESPONSE RATIO PID/FID= 0.00



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	5274.96	65611	1437643
YES	1318.74	18913	375300
YES	659.37	10562	195545
YES	119.88	0	34626
	SLOPE	12.34	270.7
	INTERCEPT	1018	11838
	CORR.COEFF.	0.9978	0.9999
RESPONSE RATIO PID/FID=		0.0456	

ISOPROPANOL

RAW DATA AND LINEAR REGRESSION

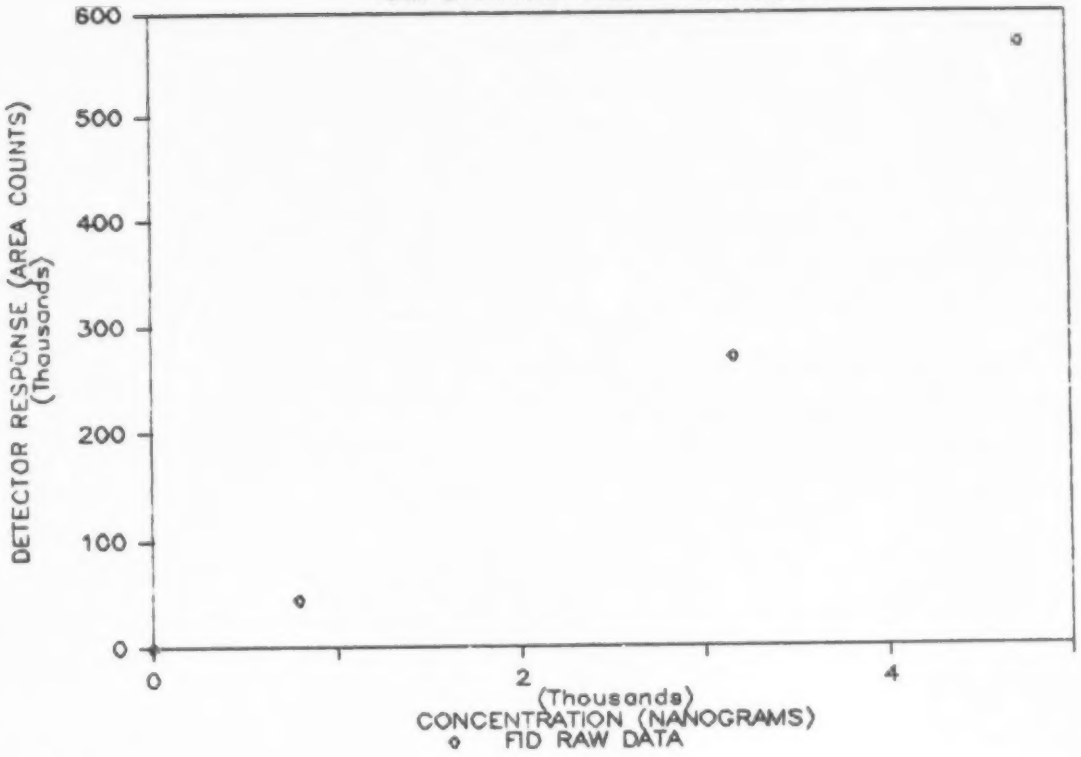


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	4713.00	147371	647690
YES	1178.25	24090	158962
YES	785.50	18949	107207
YES	107.11	3230	12303
	SLOPE	32.20	137.9
	INTERCEPT	-6208	-2336
	CORR.COEFF.	0.9963	1.0000

RESPONSE RATIO PID/FID= 0.23

METHANOL

RAW DATA AND LINEAR REGRESSION

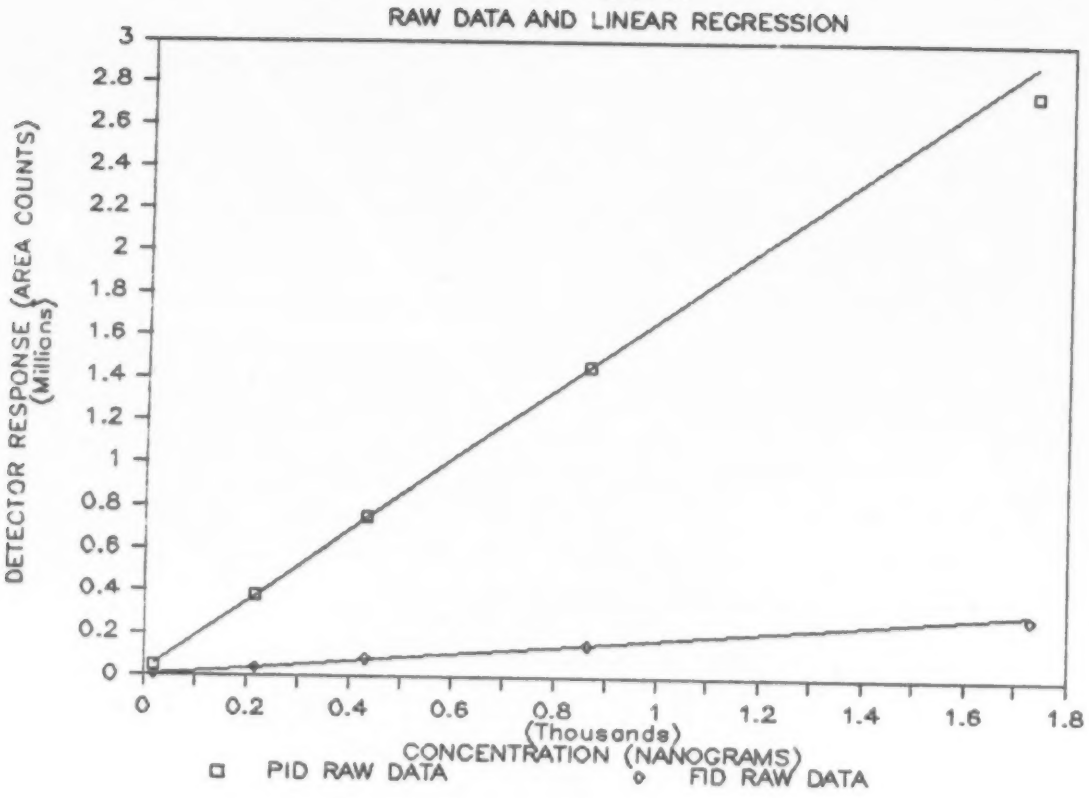


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	0.00	---	0
YES	791.40	---	44847
YES	3165.60	---	270196
YES	4748.40	---	569016
	SLOPE	---	---
	INTERCEPT	---	---
	CORR.COEFF.	---	---

RESPONSE RATIO PID/FID= ---

NOTE : DATA NOT SUITABLE FOR REGRESSION - CHROMATOGRAPHY PROBLEM.

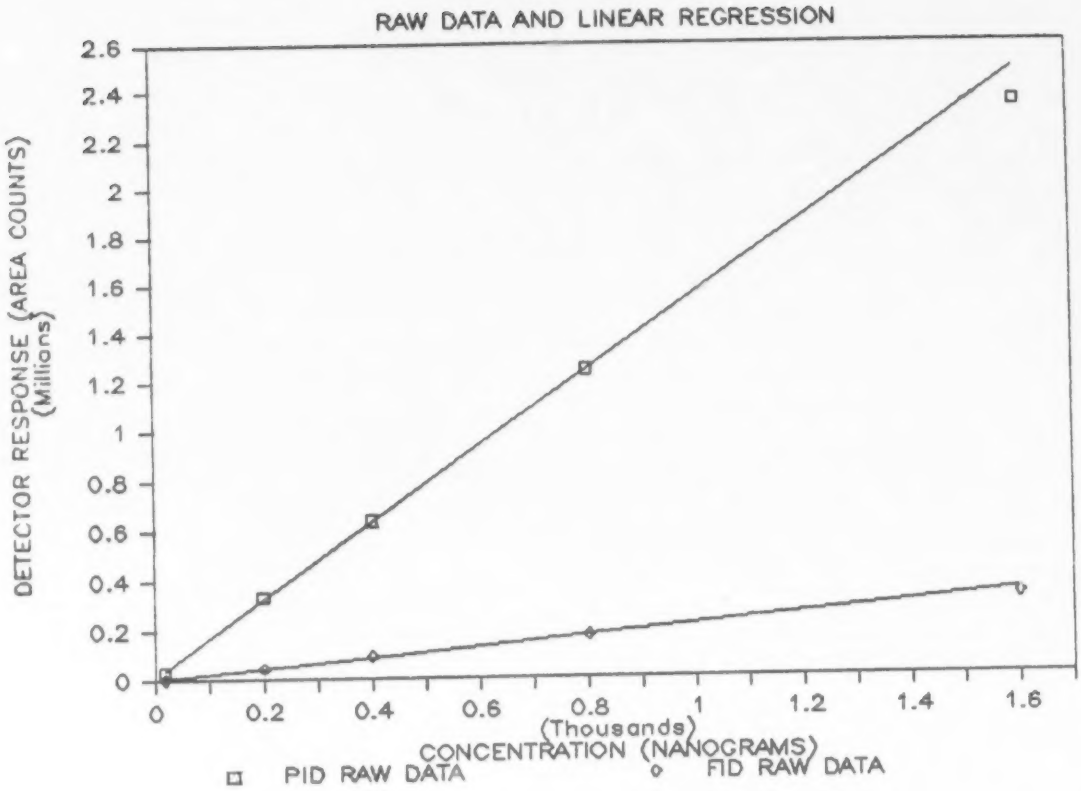
M.E.K.



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
NO	1730.80	2750530	287747
YES	865.40	1452789	155628
YES	432.70	747803	84809
YES	216.35	382522	39679
YES	19.67	49999	6629
	SLOPE	1658	177.5
	INTERCEPT	22542	3598
	CORR.COEFF.	0.9999	0.9989

RESPONSE RATIO PID/FID= 9.34

M.I.B.K.

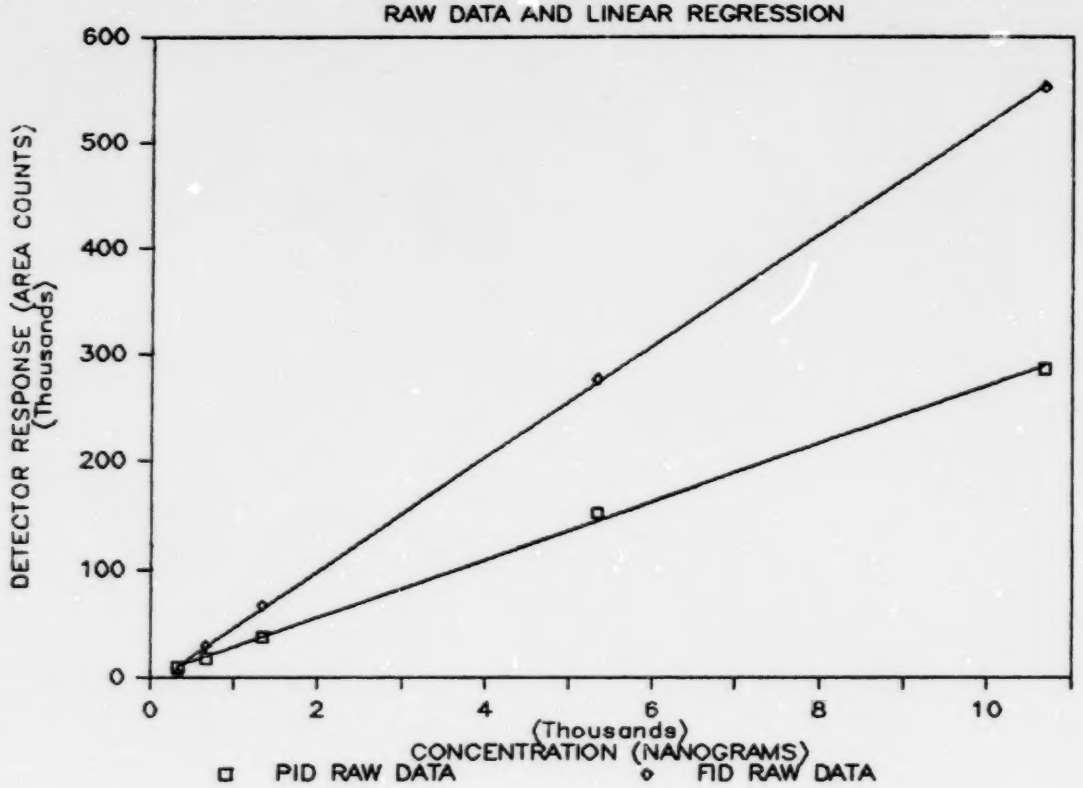


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
NO	1602.00	2343830	322551
YES	801.00	1243383	171743
YES	400.50	636020	91828
YES	200.30	334256	45402
YES	18.20	32276	4850
	SLOPE	1540	213.1
	INTERCEPT	14947	2789
	CORR.COEFF.	0.9998	0.9994

RESPONSE RATIO PID/FID= 7.22

METHYLENE CHLORIDE

RAW DATA AND LINEAR REGRESSION

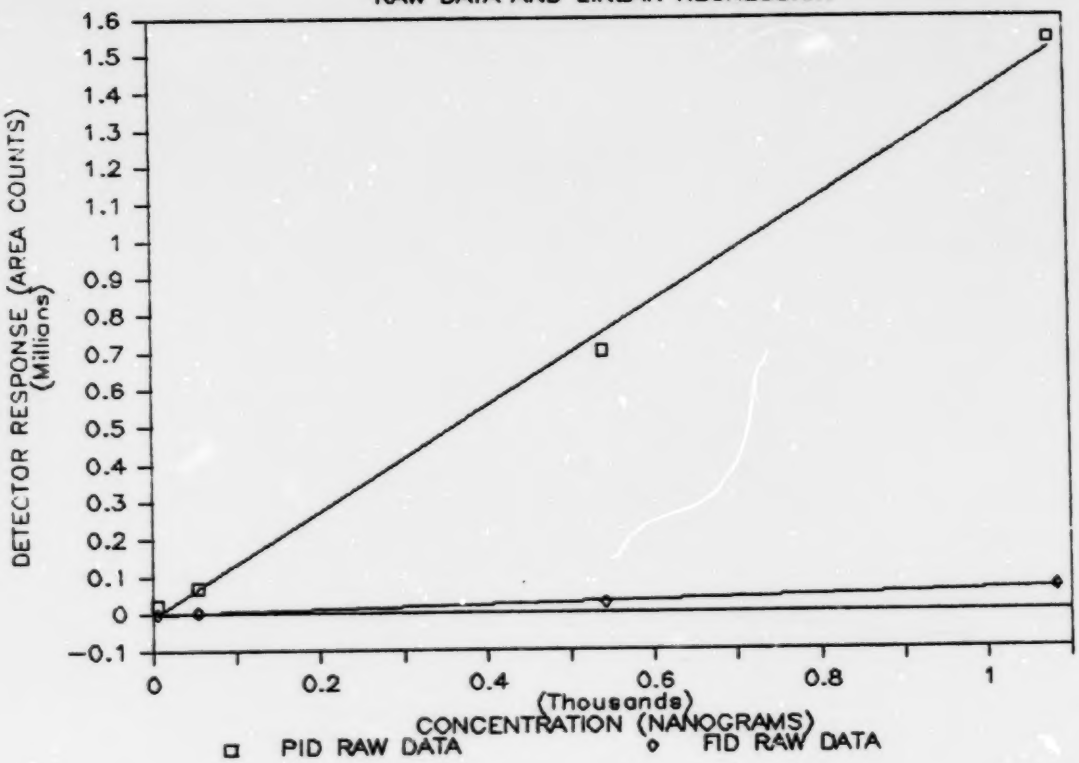


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	10680.00	286164	551936
YES	5340.00	151899	276584
YES	1335.00	38096	66893
YES	667.50	17857	30058
YES	333.75	9697	4716
	SLOPE	26.88	52.47
	INTERCEPT	2849	-6583
	CORR.COEFF.	0.9995	0.9998

RESPONSE RATIO PID/FID= 0.51

TETRACHLOROETHYLENE

RAW DATA AND LINEAR REGRESSION

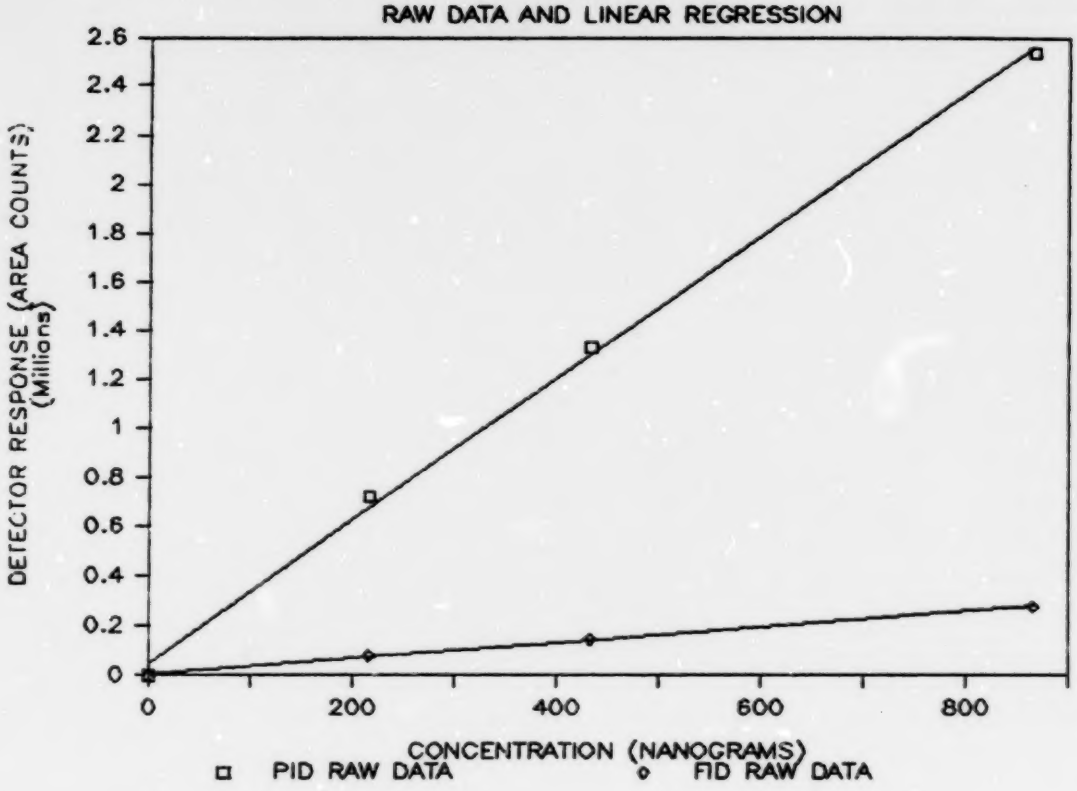


INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	5.41	23566	243
YES	54.13	68207	2500
YES	541.30	699786	26198
YES	1082.60	1536700	61678
	SLOPE	1404	56.55
	INTERCEPT	-8846	-1143
	CORR.COEFF.	0.9987	0.9970

RESPONSE RATIO PID/FID= 24.83

TOLUENE

RAW DATA AND LINEAR REGRESSION



INCL. LIN. REGR. (Y/N)	STANDARD CONCENTRATION (ng/Injection)	P.I.D. RESPONSE AVE. AREA (Area Counts)	F.I.D. RESPONSE AVE. AREA (Area Counts)
YES	0.00	0	0
YES	216.70	718014	78968
YES	433.50	1331256	142902
YES	866.90	2534437	274850
	SLOPE	2899	313.7
	INTERCEPT	46569	5198
	CORR.COEFF.	0.9992	0.9992

RESPONSE RATIO PID/FID= 9.24

APPENDIX E

TECHNICAL SPECIFICATIONS

Perkin-Elmer Manuals for
Sigma 2000 Gas Chromatograph
and 3600 Data Station

LABORATORY AND SPACE REQUIREMENTS FOR SIGMA 2000 GAS CHROMATOGRAPH

A. SPACE REQUIREMENTS

A bench or table convenient to a separately fused 20A (115V) or 10A (230V) mains power outlet is required. The power cable normally supplied is 3m (10 ft.) long. The dimensions of the instrument are shown in Figure A4-1, below, but additional space should be available adjacent to the instrument for any free-standing accessories. The instrument will be easier to install and maintain if the front, rear, and sides are readily accessible.

B. ENVIRONMENT

The laboratory conditions should meet the following requirements:

1) Laboratory Environment: Relatively clean, indoor environment, with no flammable, explosive, toxic, caustic or corrosive vapors and gases at levels that exceed Federal, State and local ordinances for continuous human exposure.

2) Ambient Temperature: 10°C to 32°C.

3) Ambient Humidity: 20 to 80% Relative Humidity with no condensation.

C. ELECTRICAL REQUIREMENTS

The line power and interconnections between instruments must fulfill the following requirements:

A) Electrical Grounding: A good earth ground is required, that is common to all instrument modules and user-supplied attachments that comprise the system. The grounding must be accomplished by a third wire in the electrical supply system. The maximum permissible resistance between the ground connections of any two units comprising a system is 0.1 ohm. The ground of the electrical supply system must be connected directly to absolute ground (earth) via the electrical supply system. The maximum permissible resistance between the ground connections of any instrument module, or user-supplied attachment, and absolute ground (earth), is 0.1 ohm.

B) Electrical Supply Quality Requirements: All electrical supplies must be within ±10% voltage tolerance of the nominal voltage for the particular instrument configuration, and are required to remain within ±10% voltage tolerance. If the nominal line voltage is not the same as the nominal instrument voltage configuration, the range of acceptable line voltages will be asymmetrical about the nominal line voltage. All supplies must be smooth, clean and free of transient voltages greater than 50V.

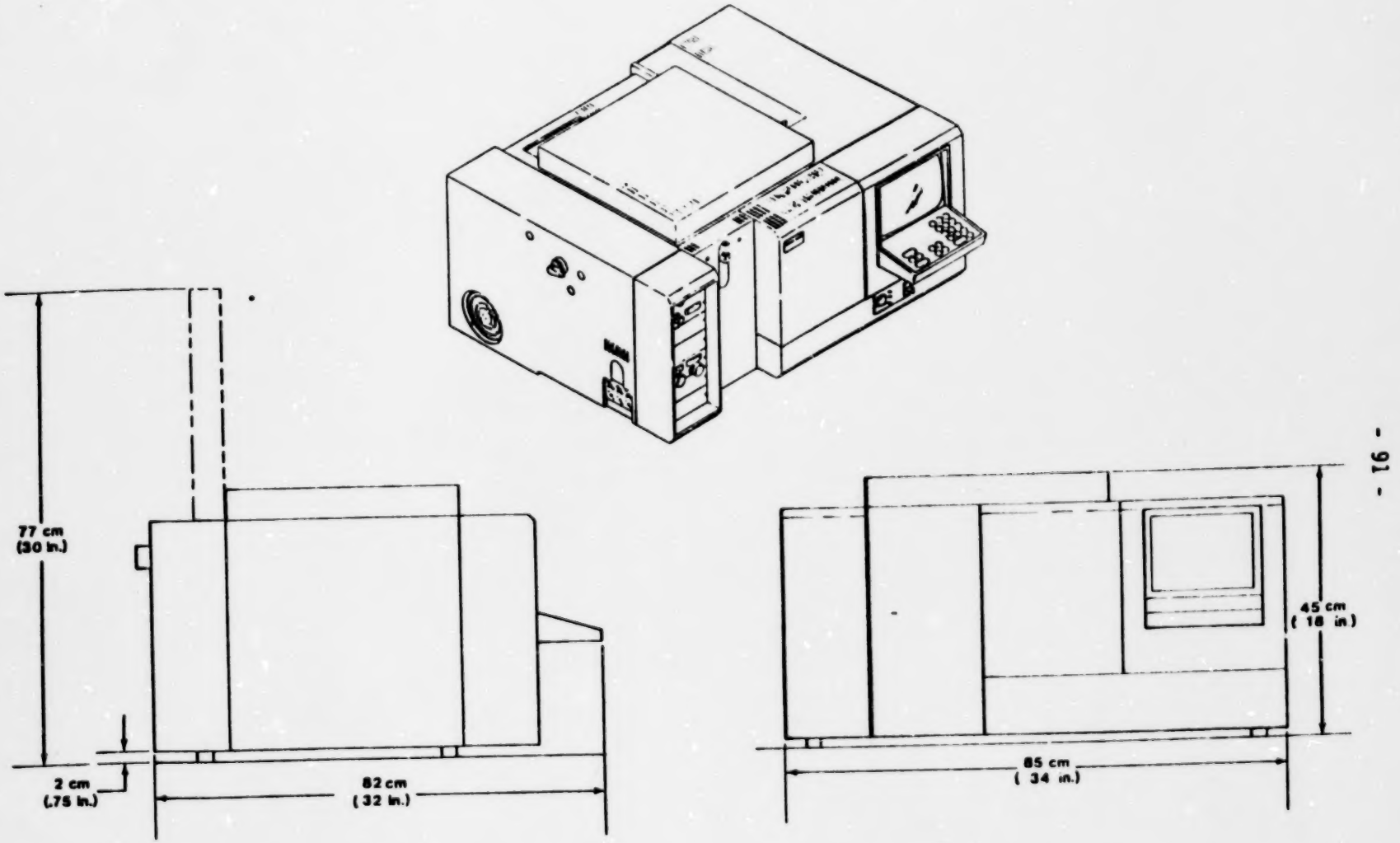


Figure A4-1 - Dimensions of the Model 2000

115V instruments should be connected to an independent 20A line. Instruments should not be attached to circuits associated with equipment of a heavy-duty nature (e.g., large motors) or large or frequent loads (e.g., photo-copying systems, discharge lamps, radio transmitters).

D. POWER REQUIREMENTS

The instrument supplied will have either of the following line power ratings, as specified in the purchase order.

a) 115V, 60 Hz, 2.0 kVA (20 amp fuse in line supply)

b) 230V, 50 Hz, 2.0 kVA Single Phase (10 amp fuse in line supply)

Connect the power cables as follows:

U.S.A.*:	Black wire to Line White wire to Neutral Green wire to Ground
U.K.**:	Brown wire to Line Blue wire to Neutral Yellow/Green wire to Earth (Ground)
230V, 2 Phase Countries:	Brown wire to +115V (AC Hot) Blue wire to -115V (AC Com) Yellow/Green wire to Ground

SPECIFICATIONS FOR 3600 DATA STATION

A. TERMINAL

A,1. Environmental Conditions and Requirements

Power:	**115V ±10% 60 Hz 100V ±10% 50 Hz or 60 Hz 230V ±10% 50 Hz or 60 Hz (Line voltage and line frequency are field-selectable by P–E Service Engineer at installation.)**
Power Consumption:	275W (approximate)
Ambient Temperature:	15 to 40 degrees Celsius (59 to 104 degrees Fahrenheit)
Ambient Humidity:	20 to 80 percent relative humidity with no condensation
Laboratory Type:	Clean indoor environment. No toxic, caustic, or corrosive vapors or gases exceeding Federal, State, or local ordinances for continuous human exposure.

A,2. Configuration and Physical Size

Type:	Modular; accomplished by three interconnected modules.
Mounting:	Bench or tabletop.
Size (nested):	48 cm wide x 57 cm deep x 52 cm high (19 in. wide x 22 1/4 in. deep x 20 1/2 in. high)
Size (Data Processing Module):	48 cm wide x 34 cm deep x 19 cm high (19 in. wide x 13 1/4 in. deep x 7 1/2 in. high)
Size (Keyboard):	48 cm wide x 23 cm deep x 9 cm high (19 in. wide x 9 in. deep x 3 1/2 in. high)
Size (Visual Display Unit):	48 cm wide x 33 cm deep x 33 cm high (19 in. wide x 13 1/8 in. deep x 13 in. high)
Weight (Total):	35.0 Kg (77 lbs.)
Weight (Data Processing Module):	17.8 Kg (39 lbs.)
Weight (Keyboard):	3.2 Kg (7 lbs.)

Weight (Visual Display Unit): 14.0 Kg (31 lbs.)

A,3. Characteristics

A,3a. Data Processing Module

Processor Type: 8-bit microprocessor, Motorola 6800-based; cycle time is 2 microseconds.

Memory: 64K bytes total (ROM and RAM):
12K to 16K bytes (ROM and RAM) for the operating system;
Variable number of bytes (RAM) for current application and data.

Disk Drives: 2 microfloppy disk drives, (80K bytes per side).

Important: Only soft sectored 5.25 inch microfloppy disks may be used.

Tracks:	40 per side
Sectors:	16
Bytes/sector:	128
Disk Capacity (formatted):	80K (163, 840) bytes (per side)
Access time:	30 milliseconds (track to track) 370 milliseconds (average) 20 milliseconds (settling time)

Power Supply:

Input: 100V/115V/230V ±10% RMS
47 to 63 Hz
275W

Output: +5V DC ±1%, 8A. (maximum) with remote sensing
+12V DC ±%, 2.75A. (maximum)
-12" DC ±5%, 1A. (maximum)

Over-voltage and short-circuit protections provided on each output.

Operating system: Operating system (PETOS) is resident in ROM.

A,3b. Keyboard

Alpha-numeric Keys: 60 keys arranged in standard ASCII format

Numeric Keys:	**12-Key-pad includes decimal point, comma, and ten numerals.**
Operation Keys:	**12-Key group provided for display and cursor control and for editing purposes.**
Special Function Keys:	**24-special function keys for use with the current application program.**
Signalling:	Keyswitch actuation is indicated by an audible tone of controllable intensity.

A,3c. Visual Display Unit

Type:	multipurpose CRT display; self-supporting with internal power supply. Permanently wired for 115V, 50/60 Hz operation.
Screen Size:	12 inches (measured diagonally)
Alpha-numeric display:	25 lines 80 alpha-numeric characters/line white image on black background
Scroll:	Upward
Cursor:	Controllable, as required by current task.

A,4. Terminal Controls (excluding Keyboard controls)

Power On-Off:	Rocker switch located on rear panel of the data processing module.
Abort:	Pushbutton microswitch located on rear panel of the data processing module.
Display Intensity:	Control knob located on the front of the visual display unit.
Audible Tone:	Control knob located on the rear panel of the keyboard.

B. GRAPHICS DISPLAY (on units provided with this option)

Horizontal Resolution:	**720 data points**
Vertical Resolution:	**250 data points**
Multiple (split screen) Display:	**3 maximum, dependent upon the application**

Special Features:

grid function, dependent upon the application;
movable cursor pair, dependent upon the application

POOR

QUALITY

ORIGINAL